

DESY SR-81/02
May 1981

AN EXAFS STUDY OF THE STRUCTURE OF
Co-Mo HYDRODESULFURIZATION CATALYSTS

by



Bjerne S. Clausen, Henrik Topsøe, Roberto Candia, Jørgen Villadsen
Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark

Bruno Lengeler
IFF, Kernforschungsanlage Jülich, D-5170 Jülich 1

Jens Als-Nielsen, Finn Christensen
Risø National Laboratory, DK-4000 Roskilde, Denmark

DESY behält sich alle Rechte für den Fall der Schutzrechtserteilung und für die wirtschaftliche Verwertung der in diesem Bericht enthaltenen Informationen vor.

DESY reserves all rights for commercial use of information included in this report, especially in case of apply for or grant of patents.

To be sure that your preprints are promptly included in the
HIGH ENERGY PHYSICS INDEX ,
send them to the following address (if possible by air mail) :

DESY
Bibliothek
Notkestrasse 85
2 Hamburg 52
Germany

An EXAFS Study of the Structure of
Co-Mo Hydrodesulfurization Catalysts.

Bjerne S. Clausen^a, Henrik Topsøe*, Roberto Candia*, Jørgen Villadsen*,
Bruno Lengeler[□], Jens Als-Nielsen⁺, Finn Christensen⁺.

* Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark

□ IFF, Kernforschungsanlage Jülich, D-5170 Jülich 1, FRG

+ Risø National Laboratory, DK-4000 Roskilde, Denmark

^a To whom queries concerning this paper should be addressed.

Abstract

By analysing the extended X-ray absorption fine structure (EXAFS) of the Mo absorption edge, structural information about both calcined and sulfided Mo/Al₂O₃ and Co-Mo/Al₂O₃ catalysts has been obtained. The calcined catalysts show only one strong backscatterer peak in the radial distribution function, which indicates that molybdenum is present in a highly disordered structure. For the Co-Mo/Al₂O₃ catalyst the presence of cobalt seems to have some effect on the immediate surroundings of molybdenum. Upon sulfiding the catalysts, an ordering of the molybdenum-containing phase takes place as evidenced by the observation of a contribution from the second coordination shell. From a comparison with EXAFS data obtained on well-crystallized MoS₂ it is concluded that the molybdenum atoms in the catalysts are present in MoS₂-like structures. Furthermore, from a comparison of the amplitude of the Mo-backscatterer peak it is found that these MoS₂-like structures are ordered in very small domains.

I. Introduction.

Hydrodesulfurization (HDS) catalysts, which are used for removal of sulfur from various fossil hydrocarbon fuels, usually consist of Mo and Co dispersed on a high surface area support such as γ -alumina. In view of their industrial importance HDS catalysts have been extensively studied by a variety of experimental techniques, and a number of hypotheses have been presented in order to describe the structure of the catalyst both in its precursor (calcined) and its active (sulfided) states. For example, for the active state of the catalyst it has been proposed that the molybdenum is present either as some type of molybdenum oxysulfide (see, e.g., 1-3) or as MoS_2 with cobalt either intercalated in the MoS_2 (4,5) or present as a separate phase of Co_9S_8 (6). Recent Mössbauer emission spectroscopy measurements (7,8) on this catalyst system have given evidence for a structure different from those mentioned above and it was proposed (7) that this structure, which contains both molybdenum, cobalt and sulfur ("Co-Mo-S" phase), mainly consists of single S-Mo-S slabs (the basic building units of MoS_2) with cobalt most probably substituting the molybdenum atoms in the structure.

Although Mössbauer spectroscopy is ideal for studying the amorphous or microcrystalline nature of the active phases present in HDS catalysts, the technique only gives direct information on the location of the cobalt atoms. In order to obtain structural information on the molybdenum atoms in the catalysts an investigation has been undertaken using extended X-ray absorption fine structure (EXAFS). This technique has recently attracted much attention in studies of catalysts since it allows a determination of local structural parameters like coordination number and interatomic distances, and it has therefore been used in order to arrive at a structural description of "X-ray amorphous" systems (see, e.g., 9-11).

II. Experimental.

The preparation of the HDS catalysts has been reported previously (8) and only a few details will be given here. The $\text{Mo}/\text{Al}_2\text{O}_3$ (8.6% Mo) catalyst was prepared by impregnating $\gamma\text{-Al}_2\text{O}_3$ (250 m^2/g) with ammonium heptamolybdate followed by drying and calcining in air at 775 K for 2 h. The Co-Mo/ Al_2O_3 (Co/Mo = 0.6 atomic ratio) catalyst was prepared by adding cobalt nitrate to the above $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst, and then by drying and calcining in air at 775 K for 2 h. A reference material of well-crystallized MoS_2 was obtained from Riedel-de Haën AG (surface area (BET) = 1.79 m^2/g ; crystallite dimension obtained from the X-ray diffraction (002) reflection: $D(002) \sim 650 \text{ \AA}$).

The $\text{Mo}/\text{Al}_2\text{O}_3$ and the Co-Mo/ Al_2O_3 catalysts in the calcined state and the well-crystallized MoS_2 were pressed into self-supporting wafers, 1 1/8" in diameter, and mounted between two pieces of Magic tape. The sulfided alumina-supported catalysts were studied *in situ* by placing wafers (16 mm in diameter) in a specially designed cell equipped with X-ray transparent windows. Sulfidation of the samples was carried out in the cell in a gas mixture of $\text{H}_2/\text{H}_2\text{S}$ (2% H_2S) at 675 K for 4 h after which treatment the cell was sealed off. The absorber thickness, x , of the samples was chosen such that $\mu x \sim 1$ (μ is the linear absorption coefficient) on the high-absorption side of the edge. The EXAFS experiments were performed at DESY in Hamburg using the synchrotron radiation from the DORIS storage ring and the EXAFS-setup at EMBL (12). The X-rays, which were emitted by the storage ring at about 4.6 GeV with a typical current of 10 mA, were monochromatized by two Si (220) single crystals and the beam intensity was measured, before (I_0) and after (I) passing through the sample, by use of two ionization chambers filled with Ar. All spectra were obtained at room temperature at 2 eV steps extending up to 1000 eV above the K-edge of Mo.

III. Results.

The raw EXAFS data for the alumina-supported catalysts in the calcined state are shown in Figure 1, where $\mu x = \ln(I_0/I)$ is plotted against photon energy. The EXAFS data analysis used here has been described in detail in reference (13). This procedure involved a background subtraction by means of cubic spline functions, multiplication of the EXAFS by a factor k , and normalization by the jump height at the K-edge. The structural environment of the Mo atoms in the two catalysts as determined by Fourier inversion of the EXAFS data is shown in Figure 2 where R is the radial distance from the absorbing Mo atom. The radial distribution function for both catalysts shows the presence of only one distinct backscatterer peak, which is undoubtedly due to oxygen. Applying the principle of transferability of phase shifts (14) a Mo-O interatomic distance of about 1.73 Å can be estimated by use of a scattering phase shift of 0.44 Å (15) for the Mo-O atom pair.

Figure 3 a-c shows the EXAFS spectra for well-crystallized MoS₂ (a) and the sulfided catalysts, Mo/Al₂O₃ (b) and Co-Mo/Al₂O₃ (c), the latter two being obtained *in situ* in the H₂/H₂S mixture. The corresponding Fourier inversions of the data are shown in Figure 4 a-c. It is observed that the peak due to the first coordination shell is located at essentially the same R -value (~ 1.90 Å) and has the same amplitude in all three cases. The location of the peak due to the second coordination shell ($R \sim 2.86$ Å) is also found to essentially identical in all the samples. However, the amplitude of the peak associated with this shell is substantially lower in the catalysts (Fig. 4 b and c) and that found in the well-crystallized MoS₂ (Fig. 4 a).

A region surrounding each of the two main peaks in R -space was also transformed back into k -space for the transforms shown in Figure 4. The results of this Fourier filtering procedure showed that in all three cases the EXAFS amplitude due to backscatterer atoms in the first coordination shell

has a maximum located at a relatively low k -value (about 4.5 \AA^{-1}) whereas the second shell gives a maximum located at a higher k -value (about 9 \AA^{-1}). These results indicate that the first peak in the Fourier transforms is caused by low Z atoms and the second peak by high Z atoms (15-17), which suggests that these peaks are due to scattering from S and Mo, respectively. This is in agreement with the structure of MoS₂ which has sulfur in the first coordination shell and molybdenum in the second shell.

The nearest Mo-S and Mo-Mo interatomic distances in MoS₂ are 2.41 Å and 3.16 Å, respectively. By use of these values and the peak positions from the Fourier transform of well-crystallized MoS₂ (Fig. 4 a), empirical phase shifts for Mo-S and Mo-Mo scattering can be determined. The results are $\alpha_{\text{Mo-S}} \approx 0.51 \text{ \AA}$ and $\alpha_{\text{Mo-Mo}} \approx 0.30 \text{ \AA}$, and these values are in qualitative agreement with those published by Cramer *et al.* (15).

In contrast to the sulfided catalysts the radial distribution function for the well-crystallized MoS₂ (Fig. 4 a) also seems to show peaks which may be identified as originating from coordination shells outside the second one. No great differences are observed between the results of the Mo/Al₂O₃ and the Co-Mo/Al₂O₃ catalysts in the sulfided state.

IV. Discussion.

The present EXAFS data show that for the Mo/Al₂O₃ and Co-Mo/Al₂O₃ catalysts in the calcined (oxidic) state their radial distribution functions have only a single strong backscatterer peak due to oxygen atoms surrounding the molybdenum. The absence of more distinct peaks suggests that a great deal of disorder exists outside the first coordination sphere of the molybdenum atom. Schuit and coworkers (1) have suggested the presence of a "MoO₃-monolayer" structure on the surface of the alumina in calcined catalysts. However such a structure would presumably give rise to some degree of order outside the first coordination shell which is not observed in the present study.

This shows that there does not exist a single well-defined molybdenum-containing compound. Rather, the results suggest that in the calcined catalyst molybdenum is present as isolated ions, chains, or small disordered patches.

The Mo-O bond length of about 1.73 Å, calculated from the peak position and the empirical phase shift published by Cramer *et al.* (15), is within those Mo-O distances exhibited for tetrahedral-coordinated Mo in $\text{Fe}_2(\text{MoO}_4)_3$ and is also in accordance with the shorter of the Mo-O distances in CoMoO_4 and MoO_3 , in which Mo is octahedrally coordinated. By use of other spectroscopic techniques (see, e.g., 18-20) it has been reported that Mo is present both tetrahedrally and octahedrally coordinated, in the calcined state of Co-Mo/ Al_2O_3 catalysts. From the present results it is not possible to obtain direct information about the coordination number of the molybdenum atoms but such information could be obtained from a more detailed EXAFS study involving studies of several model compounds, which allow to obtain accurate phase shifts and amplitude functions for the samples in question.

By comparing the radial distribution functions for the Mo/ Al_2O_3 and the Co-Mo/ Al_2O_3 catalysts it is found that the Mo-O distance in both samples is essentially the same. However, the backscatterer peak is broader in the Co-Mo/ Al_2O_3 catalyst, which may suggest that the presence of cobalt has some effect on the immediate surroundings of the absorbing molybdenum atoms. Such a result could be in accordance with several studies (see, e.g. 20-23) which have shown that in calcined catalysts there may exist an interaction between cobalt and molybdenum possibly originating from the presence of cobalt-molybdate like phases. However, the present results show that the latter phases, if present, are not as well ordered as bulk CoMoO_4 .

It may be worthwhile to mention the shape of the absorption edge itself. In the absorption spectra in Figure 1 it is clearly observed that a low energy shoulder is superimposed on the rising curve of the main peak. This shoulder can be interpreted as originating from the $1s \rightarrow 4d$ transition (24). By studying a series of Mo complexes with different sulfur and oxygen ligands, Cramer (24) has found that this transition is particularly intense when molybdenum is doubly bound to oxygen.

In contrast to the calcined catalysts the Mo K-edge of MoS_2 and the sulfided catalysts does not show a low energy shoulder due to the $1s \rightarrow 4d$ transition. In (24) it was found that this transition is virtually non-existent when molybdenum has all sulfur ligands in a non-tetrahedral coordination. It is therefore likely that the major fraction of the molybdenum atoms in the sulfided catalysts are present in a sulfided environment and not as an oxysulfide as suggested by several authors (1-3). Further support for this view is given below.

The EXAFS data for the Mo/ Al_2O_3 and Co-Mo/ Al_2O_3 catalysts in the sulfided state show that some degree of order exists outside the first coordination shell because two distinct backscatterer peaks are observed in the Fourier transforms of these catalysts (Figure 4 b and c). The fact that the position as well as the magnitude of the first peak are essentially the same for well-crystallized MoS_2 and for the two sulfided catalysts strongly indicates that the molybdenum in the catalysts has the trigonal prismatic sulfur coordination as in bulk MoS_2 . This suggests that a MoS_2 -like phase is present in both the sulfided Mo/ Al_2O_3 and the Co-Mo/ Al_2O_3 catalysts in the sulfided state.

With respect to the second peak, similar bond lengths were found for the three samples further supporting the presence of a MoS_2 -like structure in the catalysts. However, the ratio between the second and the first peak

amplitudes is significantly lower in the catalysts than in the well-crystallized MoS_2 sample. This result indicates either that the number of Mo backscatterer atoms in the second shell in the alumina-supported catalysts is less than the number of Mo atoms present in bulk MoS_2 , or that the MoS_2 structure in the catalysts has some degree of disorder outside the first coordination shell. In view of the highly dispersed structures present in the catalysts both explanations are possible. By use of the effective phase shift and the observed peak height normalized to the number of scatterers and their distance, as determined from the second peak of the Fourier transform of bulk MoS_2 (Fig. 4 a), the average number of Mo scatterers at the distance corresponding to the second shell in MoS_2 can be estimated for the two catalysts. From the results in Figure 4 b and c it is found that the second-shell coordination number for both the $\text{Mo}/\text{Al}_2\text{O}_3$ and the $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts is around 3. This indicates that the size of domains, in which an order similar to that found in MoS_2 exists, is about 10 Å. Thus the structure in sulfided alumina-supported catalysts may be thought of as very small, ordered domains with a MoS_2 -like structure.

The present results for the sulfided catalysts are in accordance with the recent Mössbauer results (7) which showed that the active $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts contain MoS_2 -like structures in a highly dispersed state. In the latter study it was furthermore proposed that cobalt may substitute molybdenum in such structures. The present results are consistent with this proposal but provide of course no direct confirmation. This must await EXAFS studies on the Co-edge, which are now being undertaken.

V. Conclusion.

The present EXAFS study shows that the molybdenum atoms in the calcined state of alumina-supported HDS catalysts are present in structures where no significant order exists outside the first oxygen coordination shell. These

structures may be viewed as Mo atoms present as, for example, isolated ions, chains, or very small patches. In the active, sulfided state of the catalysts the immediate surroundings of the Mo atoms are identical to those in bulk MoS_2 with Mo trigonally prismatic-coordinated to sulfur. The results show that, upon sulfiding the catalysts, an ordering of the molybdenum-containing phase takes place as evidenced by the observation of a Mo-Mo distance. However, the average coordination number in this shell is lower than that found in well-crystallized MoS_2 . These results suggest that the MoS_2 -like domains formed upon sulfiding are still very small

Acknowledgement.

The authors are grateful to HASYLAB for offering beam time on the synchrotron radiation facility and to EMBL for the access to the EXAFS spectrometer. The assistance of J. Bordas and J.C. Phillips in performing the EXAFS experiments is greatly acknowledged. We would also like to thank J.W. Hansen for help in the preparation of the samples.

References

1. G.C.A. Schuit and B.C. Gates, *AIChE J.* **19**, 417 (1973).
An updated version of this article was given by B.C. Gates, J.R. Katzer, and G.C.A. Schuit, in "Chemistry of Catalytic Processes", Chapter 5, McGraw-Hill, Inc., New York, 1979.
2. F.E. Massoth, *J.Catal.* **36**, 164 (1975).
3. P.C.H. Mitchell and F. Trifiro, *J.Catal.* **33**, 350 (1974).
4. R.J.H. Voorhoeve and J.C.M. Stuijver, *J.Catal.* **23**, 243 (1971).
5. A.L. Farragher and P. Cossee, *Proc. Int. Congr. Catal.*, 5th, p. 1301 (1973).
6. B. Delmon, *Am. Chem. Soc., Div. F. L. Chem., Prepr.* **22**, 503 (1977).
7. H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, and S. Mørup, *J.Catal.* **68**, 1981 (in press).
8. C. Wivel, R. Candia, B.S. Clausen, S. Mørup, and H. Topsøe, *J.Catal.* **68**, 1981 (in press).
9. J.H. Sinfelt, G.H. Via, and F.W. Lytle, *J. Chem. Phys.* **68** (4), 2009 (1978).
10. R.M. Friedman, J.J. Freeman, and F.W. Lytle, *J.Catal.* **55**, 10 (1978).
11. F.W. Lytle, G.H. Via, and J.H. Sinfelt, in "Synchrotron Radiation Research" (S. Doniach and H. Winick, eds.) Plenum Press, Ch. 12, 1979.
12. The EXAFS spectrometer at EMBL designed by J. Bordas and J.C. Phillips.
13. B. Lengeler and P. Eisenberger, *Phys. Rev. B* **21**, 4507 (1980);
P. Eisenberger and B. Lengeler, *Phys. Rev. B* **22**, 3551 (1980).
14. P.H. Citrin, P. Eisenberger, and B.M. Kincaid, *Phys. Rev. Lett.* **36**, 1346 (1976).
15. S.P. Cramer, K.O. Hodgson, E.I. Stiefel, and W.E. Newton, *J. Am. Chem. Soc.* **100**, 2748 (1978).
16. P.A. Lee and G. Beni, *Phys. Rev. B* **15**, 2862 (1977).
17. B.-K. Teo, P.A. Lee, A.L. Simons, P. Eisenberger, and B.M. Kincaid, *J. Am. Chem. Soc.* **99**, 3854 (1977).
18. N. Giordano, J.C.J. Bart, A. Vaghi, A. Castellan, and G. Martinotti, *J.Catal.* **36**, 81 (1975).
19. H. Knözinger and H. Jeziorowski, *J. Phys. Chem.* **82**, 2002 (1978).
20. J. Medema, C. van Stam, V.H.J. de Beer, A.J.A. Konings, and D.C. Koningsberger, *J.Catal.* **53**, 386 (1978).
21. J. Grimblot and J.P. Bonelle, *J. Electron Spectrosc. Relat. Phenom.* **9**, 449 (1976).
22. R. Moné, Int. Conf. on the Scientific Basis for the Preparation of Solid Catalysts (Brussels) D3, 1975.
23. N. Topsøe, *J.Catal.* **64**, 235 (1980).
24. S.P. Cramer, SSRL Report 7807, June 1978.

FIGURE 1 K-edge absorption coefficient of Mo versus X-ray photon energy for the calcined catalysts. a) Mo/Al₂O₃ catalyst; b) Co-Mo/Al₂O₃ catalyst. Edge-structure shown in insert.

FIGURE 2 Relative magnitude of the Fourier transforms of the data in Fig. 1 after multiplication by k and background subtraction. a) Mo/Al₂O₃ catalyst; b) Co-Mo/Al₂O₃ catalyst.

FIGURE 3 K-edge absorption coefficient of Mo versus X-ray photon energy for well-crystallized MoS₂ (a); sulfided Mo/Al₂O₃ catalyst (b); and sulfided Co-Mo/Al₂O₃ catalyst (c).

FIGURE 4 Fourier transforms of the data in Fig. 3 after multiplication by k and background subtraction. a) Well-crystallized MoS₂; b) sulfided Mo/Al₂O₃ catalyst; c) sulfided Co-Mo/Al₂O₃ catalyst.

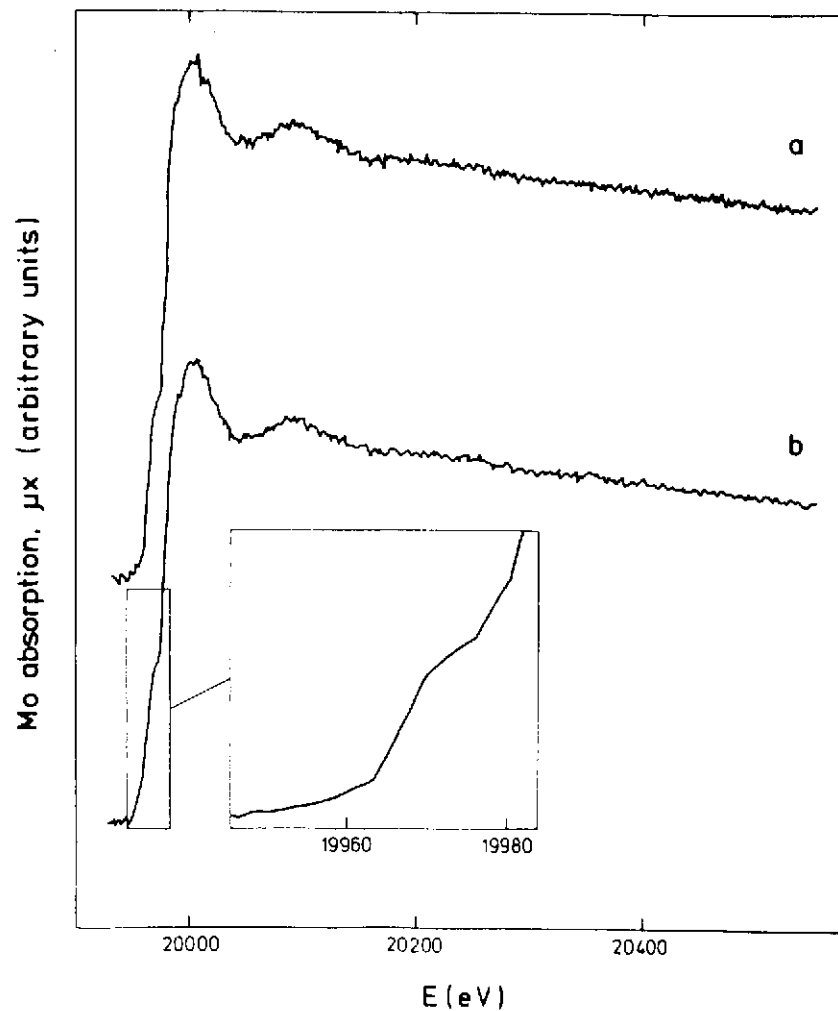


Fig. 1

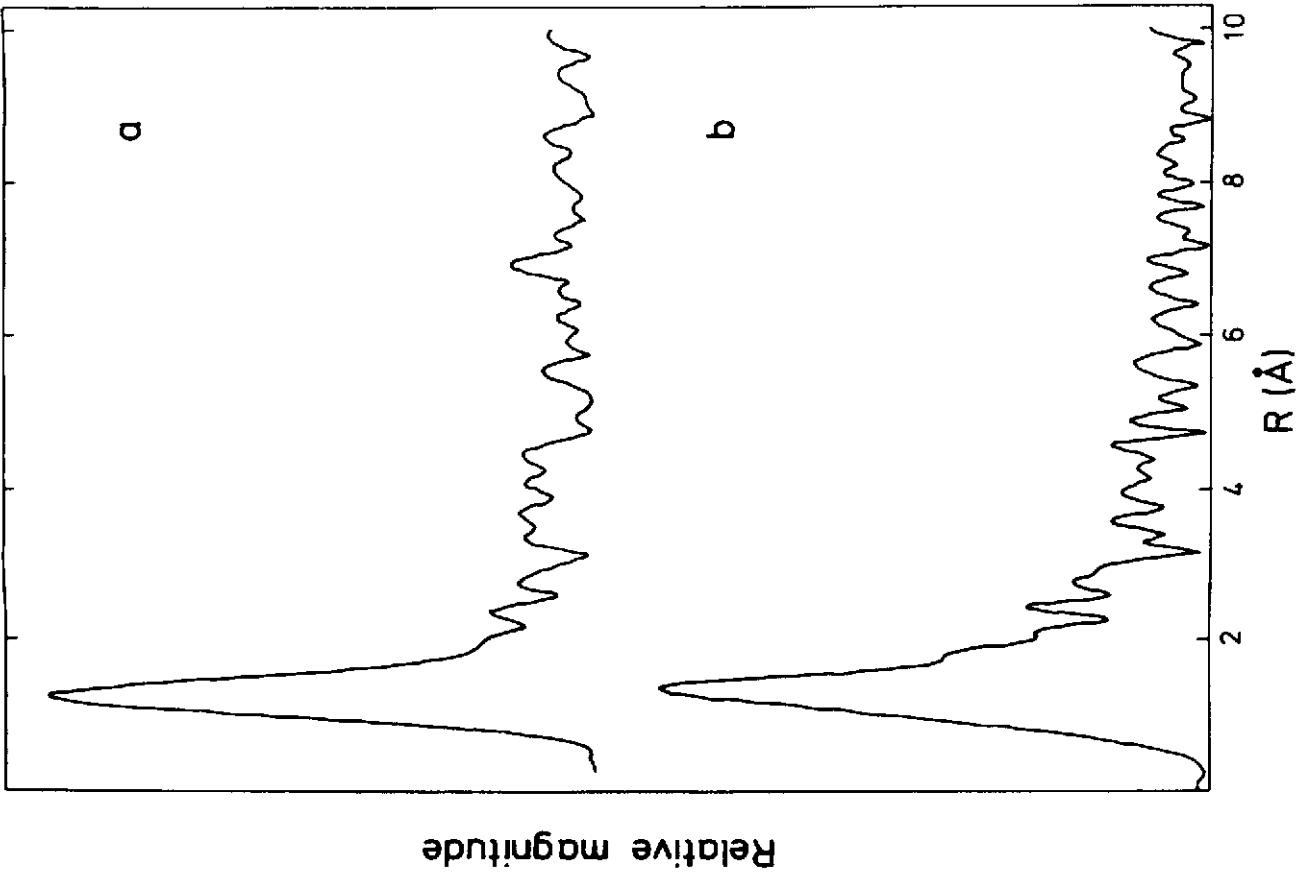


Fig. 2

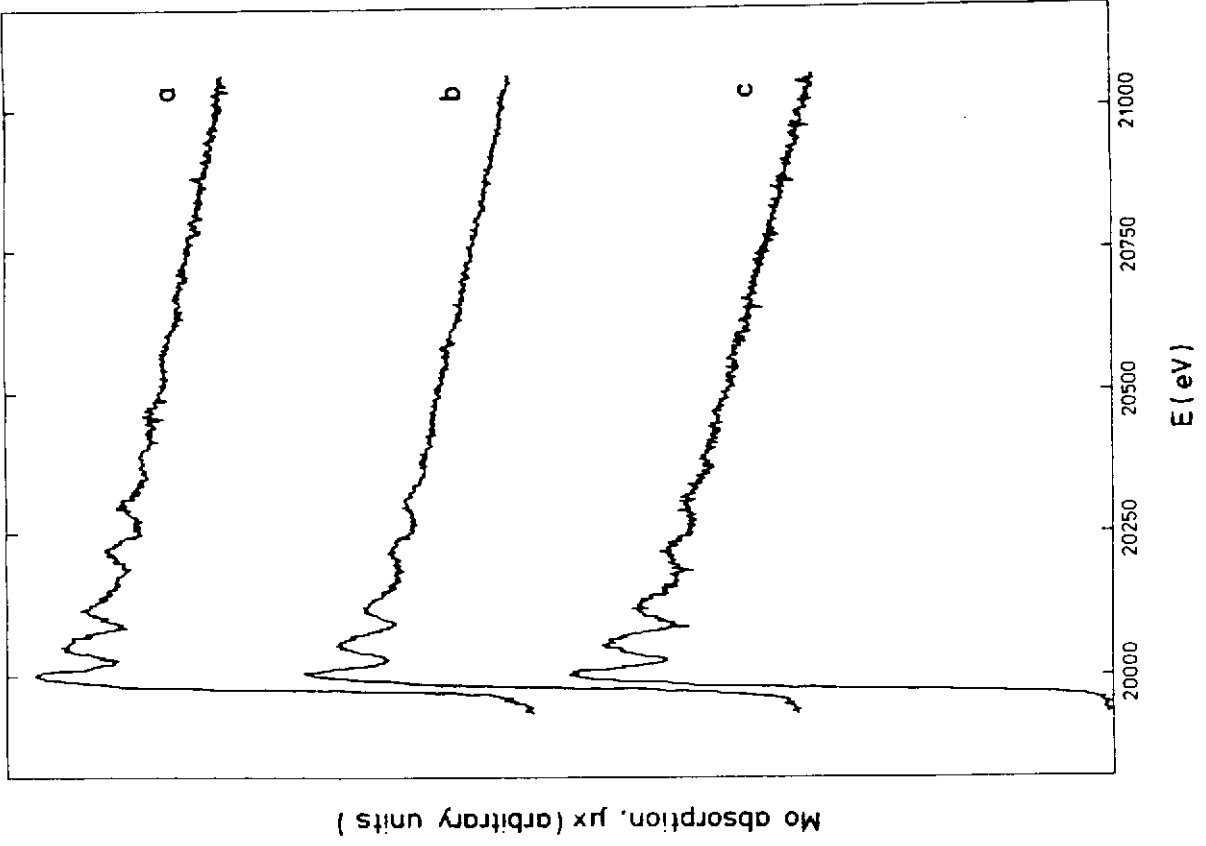


Fig. 3

