

# ISTITUTO NAZIONALE DI FISICA NUCLEARE

Sezione di Catania

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INFN/FM-90/01  
22 Gennaio 1989

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**AUGER ELECTRON SPECTROSCOPY ANALYSIS OF OXIDES**

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**ABSTRACT**

Chemical effects in Auger electron spectroscopy were investigated analysing the spectra of different oxides. A shift in the energies of the Auger electrons is the result of charge transfer and represents a measure of the valence state of an atom. A change in the peak shape of an element spectrum occurs when some of the electrons involved in this Auger process are valence electrons.

A set of collected data, in derivative spectra form, is here reported as indication of chemical shifts and shape changes of Auger peaks in the spectrometry of oxidized thin films.

## 1. - INTRODUCTION

The exact binding energy for an electron in a given element depends on the chemical environment of that element. The energy of an electron in a core state is determined by the Coulomb interaction with the other electrons and by the attractive potential of the nuclei. Any change in the chemical environment of the element will involve a spatial redistribution of the valence electron charges of this atom and the creation of a different potential as seen by a core electron. This redistribution affects the potential of the core electrons and results in a change in their binding energies. So, whenever the electron density around an atom is decreased by the transfer of electrons to another atom, the binding energies of the remaining electrons are increased. This effect produces a shift of Auger lines at lower energies.

The energy of the Auger transition  $xyz$  is given by the following relationship:

$$E_{xyz} = E_x(Z) - E_y(Z) - E_z(Z) - \{ [E_y(Z+1) - E_y(Z)] + [E_z(Z+1) - E_z(Z)] \} / 2; \quad (1)$$

where the  $xyz$  transition corresponds to an initial ionization of the  $x$  shell which hole is filled with an electron coming from  $y$  upper shell with a simultaneous emission of an other electron from the  $z$  shell to the vacuum;  $Z$  is the atomic number of the ionized atom. The first ionization produces an increasing in the energy bonding of remained electrons which is valued in the relation (1) increasing the atomic number to  $Z+1$ . If a change in the charge state of the emitting atom occurs this will produce a shift of this characteristic energy specially for the external shell electrons involved in the Auger processes [1].

The chemical energy shift is rather small and for electronegative gas, such as oxygen, chemisorbed onto a clean metal surface one would expect a shift on the order of a few eV or less.

Generally the chemical shifts can be measured using the X-ray

Photoelectron Spectroscopy (XPS) but also the Auger Electron Spectroscopy (AES) may give useful indications. Chemical shifts are more difficult to interpret in the two electron Auger process than in the one electron photoelectric process; AES line width are broaden than XPS lines, consequently XPS is typically used to explore changes in chemical binding [1]. However, Auger analysis has a good resolution and sensitivity to detect energy shift upper 0.1 eV , so it is a suitable technique to investigate on the chemical shift in oxides.

Chemical effects can produce also changes in shape of Auger peaks due, for example, to changes of electron density of occupied states of the valence band. Besides, changes in peak-to-peak intensities occur because the element concentration decrease in oxidized films according its stoichiometry.

Another significative contribution to the peak shape change can be due to the Auger electron energy loss in plasmons of the conduction electron gas. The plasmon is a quantum of a plasma oscillation and has an energy  $\hbar\omega$  of about 15-30 eV depending on the electron energy density  $N$  in the conduction band, according the following relationship:

$$\hbar\omega = \hbar(4\pi N e^2/m)^{1/2}; \quad (2)$$

where  $e$  and  $m$  represent the electron charge and electron mass, respectively.

The purpose of this work is to report a collection of AES data on the energy shifts and peak changes for some oxides of interest in electronics and biomaterials.

## 2. - EXPERIMENTAL SECTION

Experiments were performed in an ultra high vacuum (UHV) system with a base pressure in the  $10^{-10}$  Torr range. Spectra were recorded using a Varian Cylindrical Mirror Analyzer (CMA) with a coaxial electron gun. The energy resolution of 0.4% was obtained using 5 Volt peak-to-peak modulation on the CMA

external cylinder. A time constant of 100 msec was used in the phase-sensitive detector and the derivative of the electron energy distribution,  $dN(E)/dE$ , to improve the signal-to-noise ratio in the Auger spectra, were obtained with 15 min time for any sweep. All measurements were executed at room temperature; the incident beam energy was 3 KeV and the electron current 3  $\mu$ A with a spot diameter of about 10  $\mu$ m. The angle of incidence of the primary beam was 30° with respect to the normal to the surface plane of the specimen.

A set of elements, as standard samples with different atomic number, was introduced in the Auger chamber as pure and oxidized thin films (100-1000 Å in thickness) of known stoichiometry. The cleaning of the samples was performed in vacuum using repeated cycles of sputtering with 4.5 KeV argon bombardment and 0.1 mA/cm<sup>2</sup> ion current density.

Calibration of the Auger electron energy, with respect to the sample Fermi level, was achieved by the use of an elastically reflected primary electron at 2 KeV energy beam.

Surface charging, which is a common problem with thick insulating layers, became negligible using very thin films, reducing the electron beam voltage and allowing some residual surface carbon contamination to remain. Before to recorder the Auger analysis, each sample was given an argon ion bombardment dose sufficient to reduce the surface carbon contamination peak to a very low level.

Note that the measured shifts, in the energy range 1 - 20 eV, are with respect to the Fermi level of the analyzer because the sample and analyzer are in good electrical contact. Simple energy considerations show that the work function of the sample is adds in and subtract out from the measurement, so it has no effect on the measured Auger energies.

Some significant changes in the peak energy and shape of AES yield were recorded in both pure and oxidized element to understand the changes of electron distribution in the valence band states.

Changes in relative intensities between groups of Auger lines

in metal and oxide can be due to different ejection of an electron from the valence band or to decay in plasmons. Besides, changes in shape occurs also because lines separated by less than 1 eV can not be resolved so the convolution of overlapping peaks is observed.

### 3. - RESULTS

The studied elements, in atomic number order, are: Be, Mg, Al, Si, Ti, Cr, Zr, Mo, Ta and W and its oxides. Generally, chemical shifts were investigated studying the valence electron transitions to obtain measurable value of energy shifts between 1-20 eV .

Figure numbers from 1 to 10 show the AES spectra analysed at 3 KeV electron beam, in  $dN(E)/dE$  derivative form, in each pure elements and in one its oxidation state of known stoichiometry. Fig.1 shows the KLL Auger transitions in Be and BeO; the comparison shows that the main peak shift is 10 eV and that the AES spectrum shape in oxide (b) is very different in respect to the pure Be (a). The peaks at 94 and 87 eV are explained in terms of  $1s^2p^2p$  and  $1s^2s^2s$  transitions, respectively [2]. The remaining two peaks at 77 and 67 eV are due to plasmon losses from the 94 and 87 eV Auger resonance, since the bulk plasmon loss resonance is about 16 eV. Besides, the peak-to-peak intensity of the 94 eV is about a factor two lower in respect to that of 104 eV in pure Be. The decrease in the peak intensity is due to the decrease in the amount of Be atoms/cm<sup>2</sup> contained within the escape depth for the Be Auger electrons as the compound becomes richer in Oxygen.

Figures number 2, 3 and 4 show three spectra for LVV transitions in the comparisons Mg-MgO, Al-Al<sub>2</sub>O<sub>3</sub> and Si-SiO<sub>2</sub>. Fig.2 shows that the 32 eV peak in MgO oxide (b) is shifted of 13 eV at lower energy in respect to that in pure Mg at 45 eV (a) and that the peak-to-peak intensity in oxide is about a

factor two less than in pure Mg, according stoichiometry. Besides, a weak chemical shift of 8 eV in the KLL transition at 1186 eV occurs indicating that the Mg oxidation increase also the energy bonding of core electrons with consequent decreasing of KLL transitions electrons energy.

Fig.3 shows a chemical shift valued in 17 eV for LVV transition in the comparison Al-Al<sub>2</sub>O<sub>3</sub> reducing from 68 eV to 51 eV. The LVV peak-to-peak intensity is reduced by about a factor two according stoichiometry and a double peak occurs in the oxide, the second occurs to 35 eV, due to plasmon loss which is 15.3 eV in Al; a similar shift is present for deeper electron coming from KLL transitions.

Fig.4 shows a similar trend for AES comparison in Si-SiO<sub>2</sub> spectra. The main peak due to LVV transitions in Si at 92 eV (a) decreases to 76 eV in SiO<sub>2</sub> with a shift of 16 eV; the peak-to-peak intensity in oxide is reduced of about a factor three in respect to pure Si. In SiO<sub>2</sub> the variation in binding energy produces a change in the electron density of electronic states of the valence band producing two characteristic Auger peaks at 76 and 63 eV (b). The calculated plasmon energy loss, which in SiO<sub>2</sub> is about 16 eV, produces the plasmon peaks at 59 and 46 eV [3,4]. In SiO<sub>2</sub> KLL transitions also 13 eV energy shift in respect Si occurs.

Figs.5 and 6 show two spectra for MVV Auger transitions in the Ti-TiO<sub>2</sub> and Cr-Cr<sub>2</sub>O<sub>3</sub> comparisons.

In the first case the energy shift for Ti MVV main peak is 5 eV, going from 27 eV to 22 eV while for LMM peaks is of about 4 eV. In the second case the energy shift for Cr MVV and LMM main peaks is about 4 eV. The M<sub>2,3</sub>VV Auger spectra for clean and oxygen surfaces of the transition metals, like Ti, Cr, Fe, Co and Ni have been studied and results indicate a similar trend for the energy shift (3-5 eV) and shape changes. These metals have a plasmon energy of about 12 eV, so energy peaks due to plasmon energy loss occurs in the AES spectra with shifts of this quantity [5-7]. In transition metals the M<sub>2,3</sub>VV features for the oxidized surface have been interpreted in terms of

$M_{2,3}M_{4,5}$  transitions and self-ionization peaks involving electrons which have been excited from the 3p level to a localities state at the bottom of the conduction band [8].

Figs.7 and 8 show the NVV and MNN Auger spectra of clean oxidized Zr and Mo. Both  $ZrO_2$  and  $MoO_3$  oxides show that NVV and MNN energy shifts in respect the pure elements are of about 4 eV. A little energy shift of 2 eV was found also for Mo LMM transitions. When the energy shift is little, as in this case, an overlap of peaks for different valances of emitting ions may occurs and the observed spectrum in oxidized sample can be generated by summing two spectra of the Mo shape with one on the clean metal energies and the other displaced by 2 eV to lower energies. The question naturally arises as to whether atoms present in two different valence states will give an Auger spectrum showing two groups of lines separated in energy by a few eV.

Figs.9 and 10 show the NVV Auger spectra for Ta and W pure elements and a know oxide stoichiometry. A chemical shifts in NVV peaks of  $Ta_2O_5$  was measured in 3 eV for each. The triplet for the  $N_{4,5}N_{6,7}N_{6,7}$  Auger transitions at 163, 169 and 179 eV in the W elemental state are replaced by a doublet at 163 and 174 eV and a small shoulder peak at 158 eV in the  $WO_3$  state. Similar features as observed on the oxidized W film are noted in the Auger spectra of oxidized Ta film; the maximum chemical shift observed in both oxides was 5 eV [9,10].

So, as general trend, we observe that the energy shift in the valence Auger transitions decrease with the atomic number going from about 15 eV for Si to about 2 eV for Ta; the peak shapes of oxidized samples are accomplished by plasmon oscillations indicating new vibrational states of electrons in the valence band of oxidized atoms; peak-to-peak Auger intensity decrease approximatively according the element concentration in the oxidative film.

The measured shifts due to chemical bonding as detected by Auger electron energy line shifts are further confirmed by literature data [1-9].



In heavy elements, as rare earths, the Auger spectra are apparently immune to changes in chemical environment [8]. Obviously changes in oxide stoichiometry produces a change in the shape of characteristic Auger peaks because a different electron charge transfer between oxygen and element occurs. As an example, Fig.11 report the AES spectra for the system  $\text{SiO}_x$  as a function of different values of  $x$  ranging between 0 to 2. Intermediates situations to those seen for the spectra of Si and  $\text{SiO}_2$  occurs for intermediate stoichiometry.

#### 4. - CONCLUSIONS

The results reported here point out both some problems and some opportunities in the use of Auger electron spectroscopy for the study of surface regions.

The energy shifts observed when charge transfer occurs in standard oxides may help to know qualitative Auger analysis. Maximum energy shifts, of the order of 16 eV, can be found for LVV transitions for elements with atomic number of about 14; for transition metals the AES energy shifts for MVV transitions are of the order of 5 eV; for elements with atomic number upper 40 the shift is very low, about 2 eV, and for very heavy elements, with atomic number of the order of 60, it is not measurable with Auger technique.

Changes in shape of the spectra may also affect the use of Auger spectroscopy for quantitative analysis and may be used to qualitative analysis.

The most important result of this work is the observation that changes in the chemical environment of surface atoms give measurable changes in the observed AES spectra. This observation is more important because there are almost no other experimental techniques which are available to directly extract this information. Theoretically, a fairly complete picture of bonding of atoms in surface regions could be developed, but

much work remains to be done before this is accomplished. Part of the problem is a need for better sensitivity and resolution of AES technique. Such a need may be fulfilled by the development of the newer electron spectrometers coupled with the deconvolution techniques. Even with present instrumental and theoretical limitations, these results show that one can use these effect to empirically determine a great deal information about the chemical state of atoms at surfaces. The information regarding the electronic band structure change due to the bonding of elements with oxygen will be discussed in a later communication.

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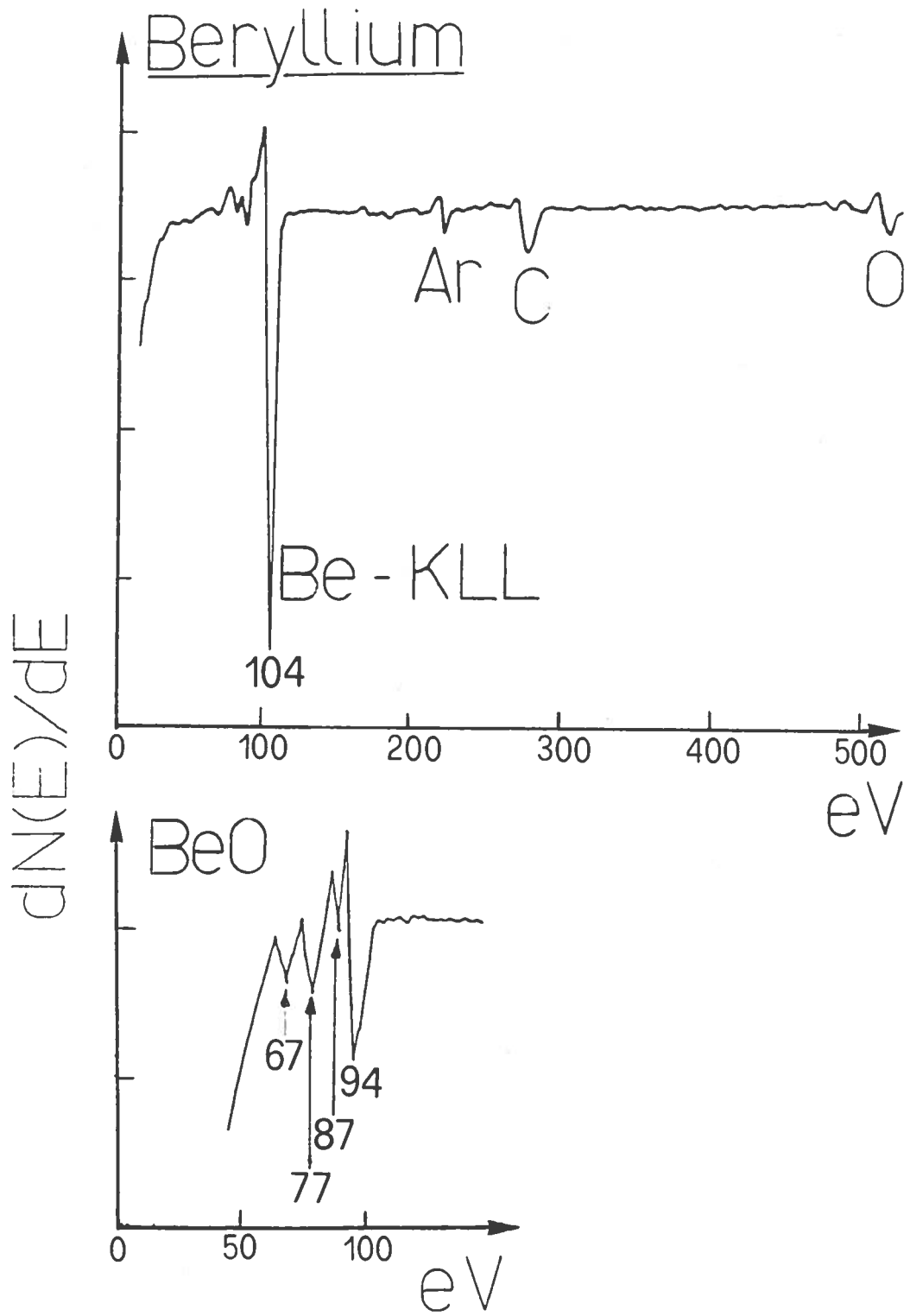


Fig. 1

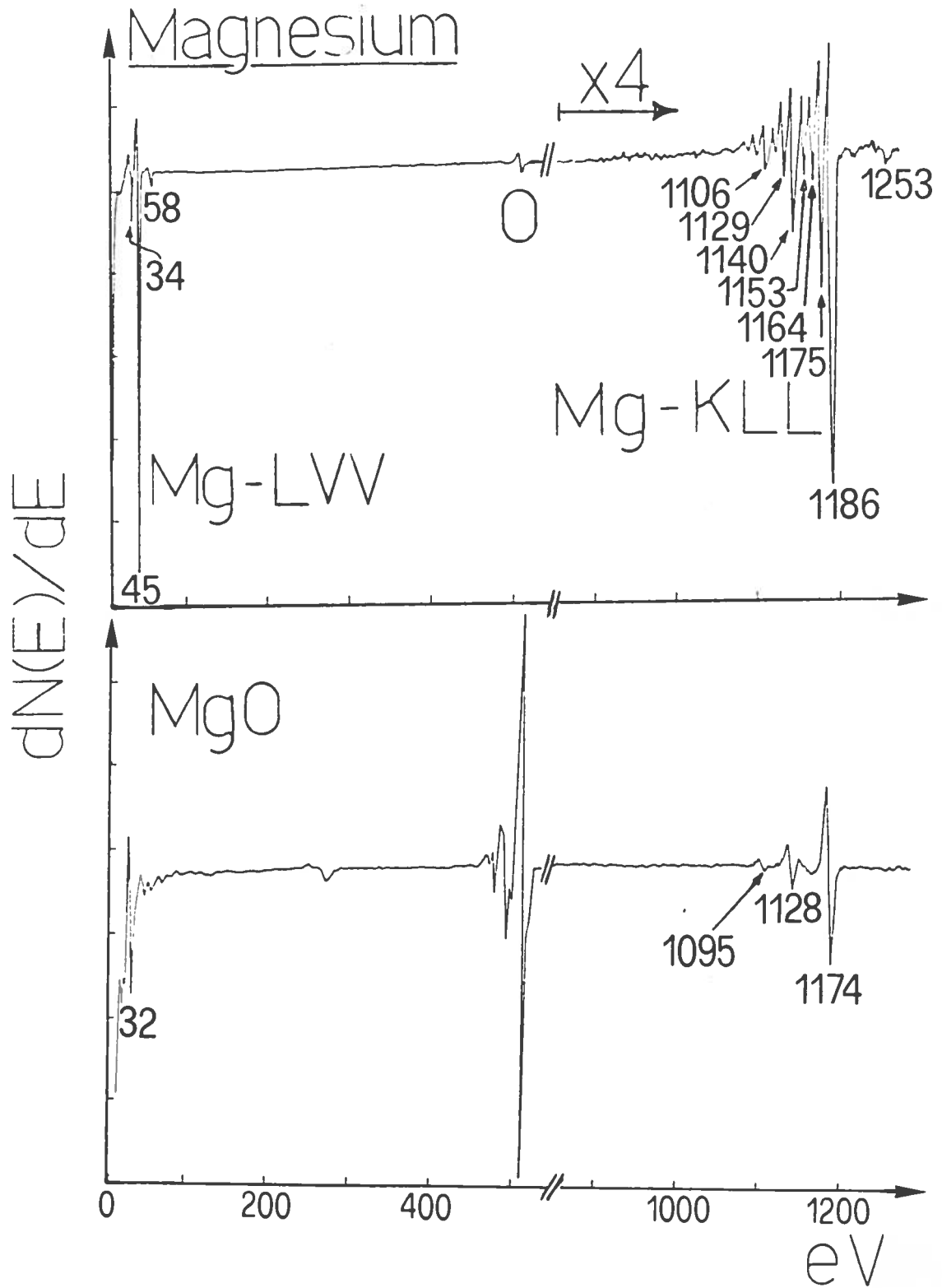


Fig. 2

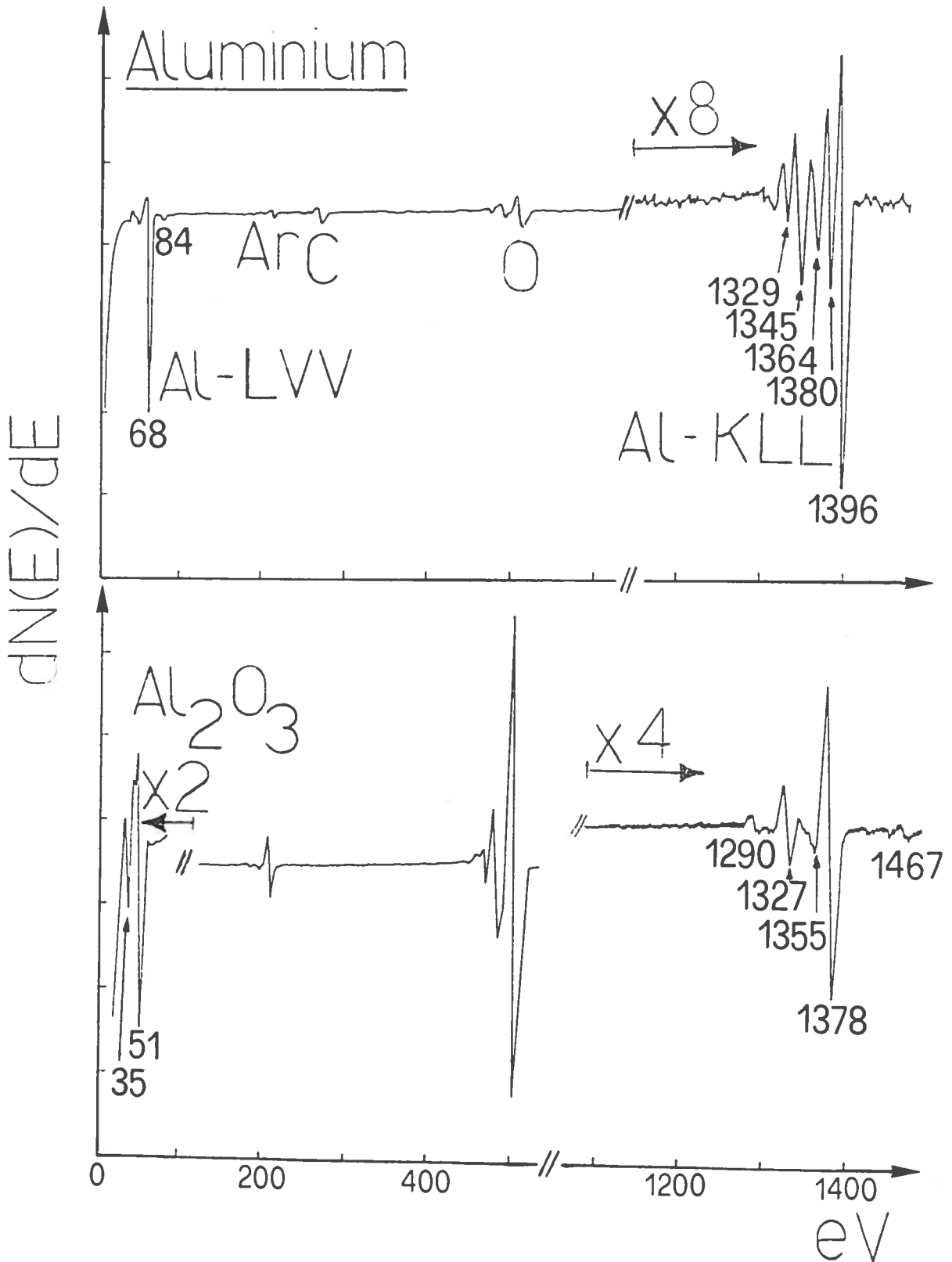


Fig. 3

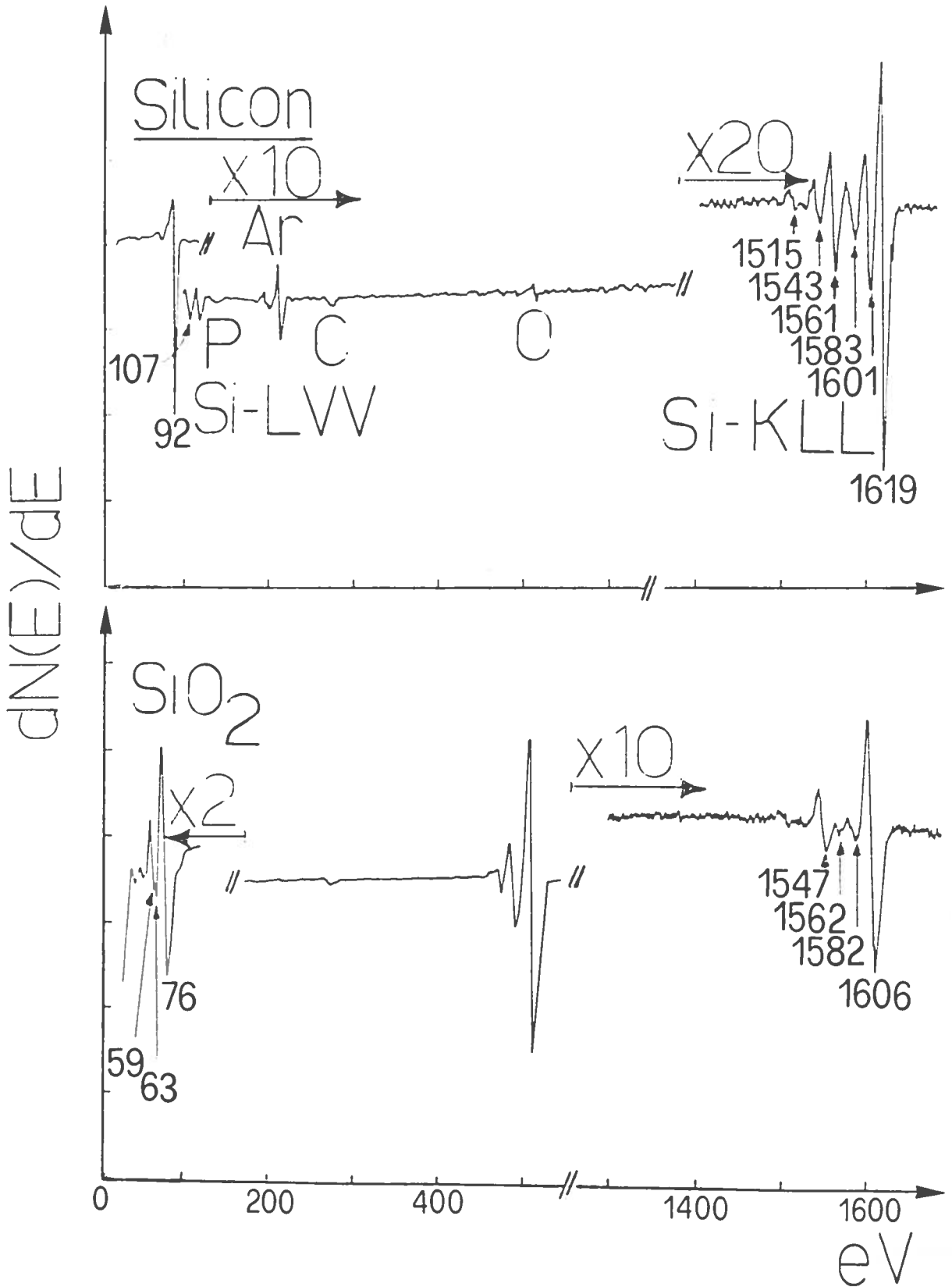


Fig. 4

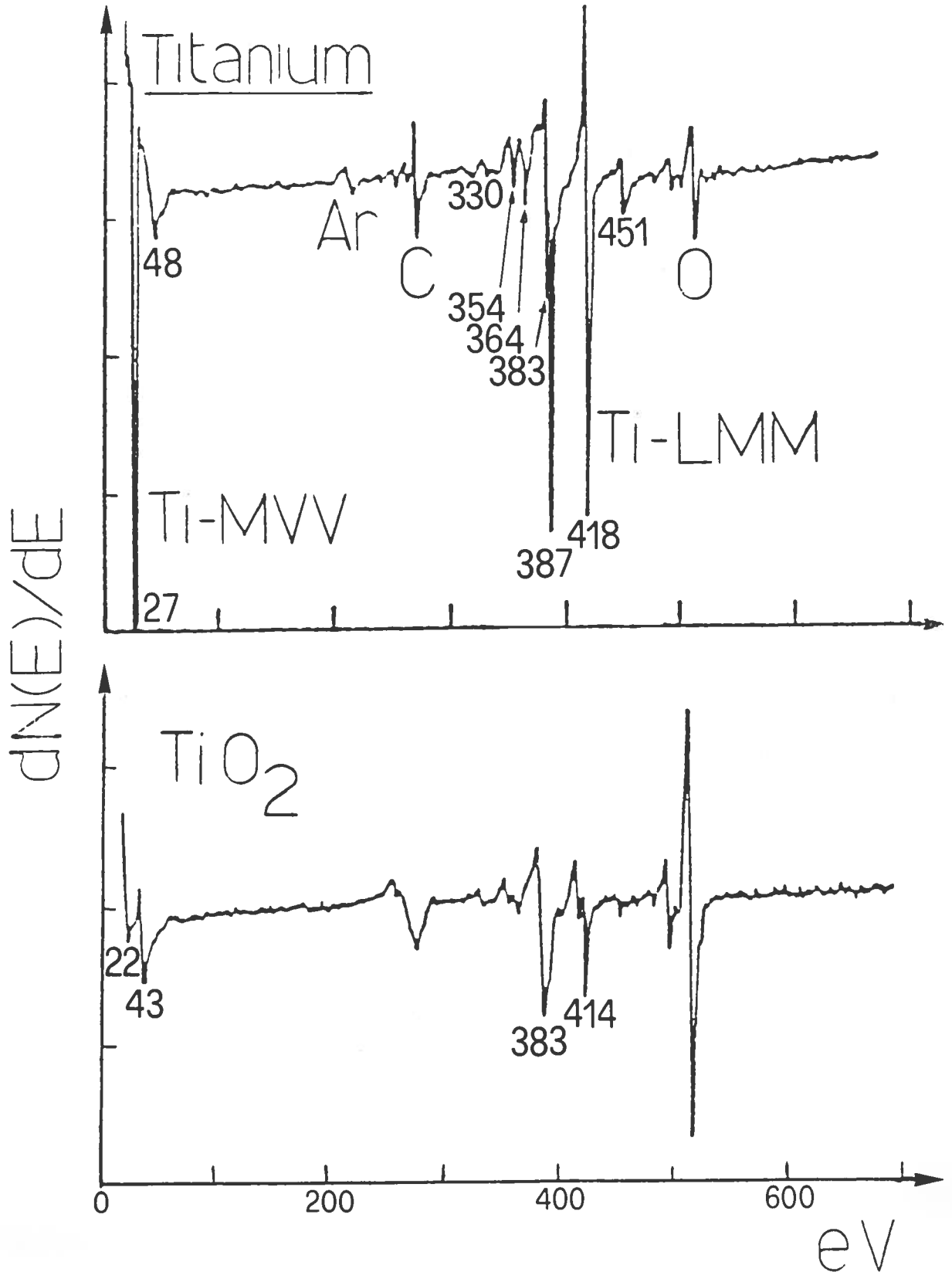


Fig. 5



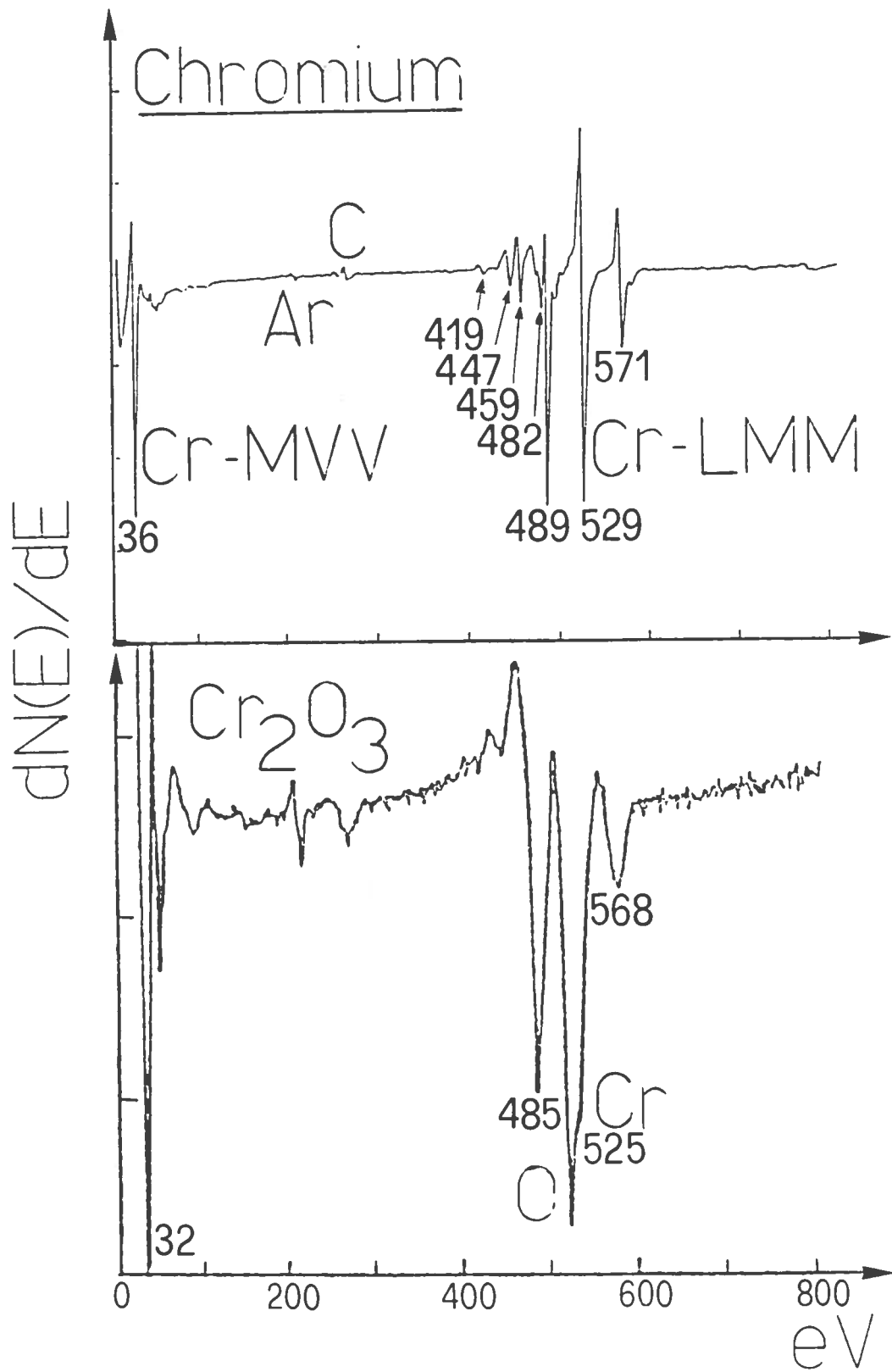


Fig. 6

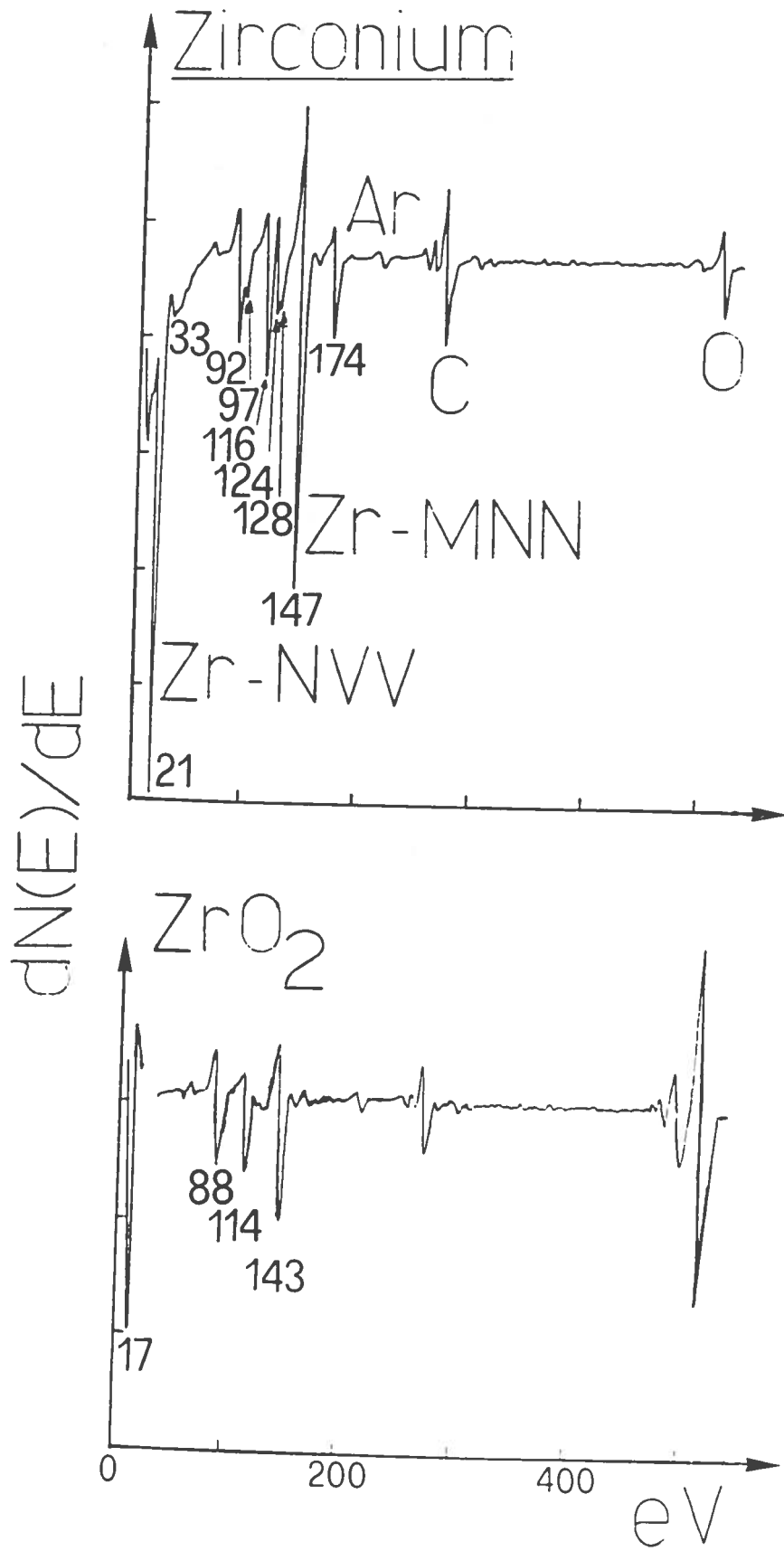


Fig. 7

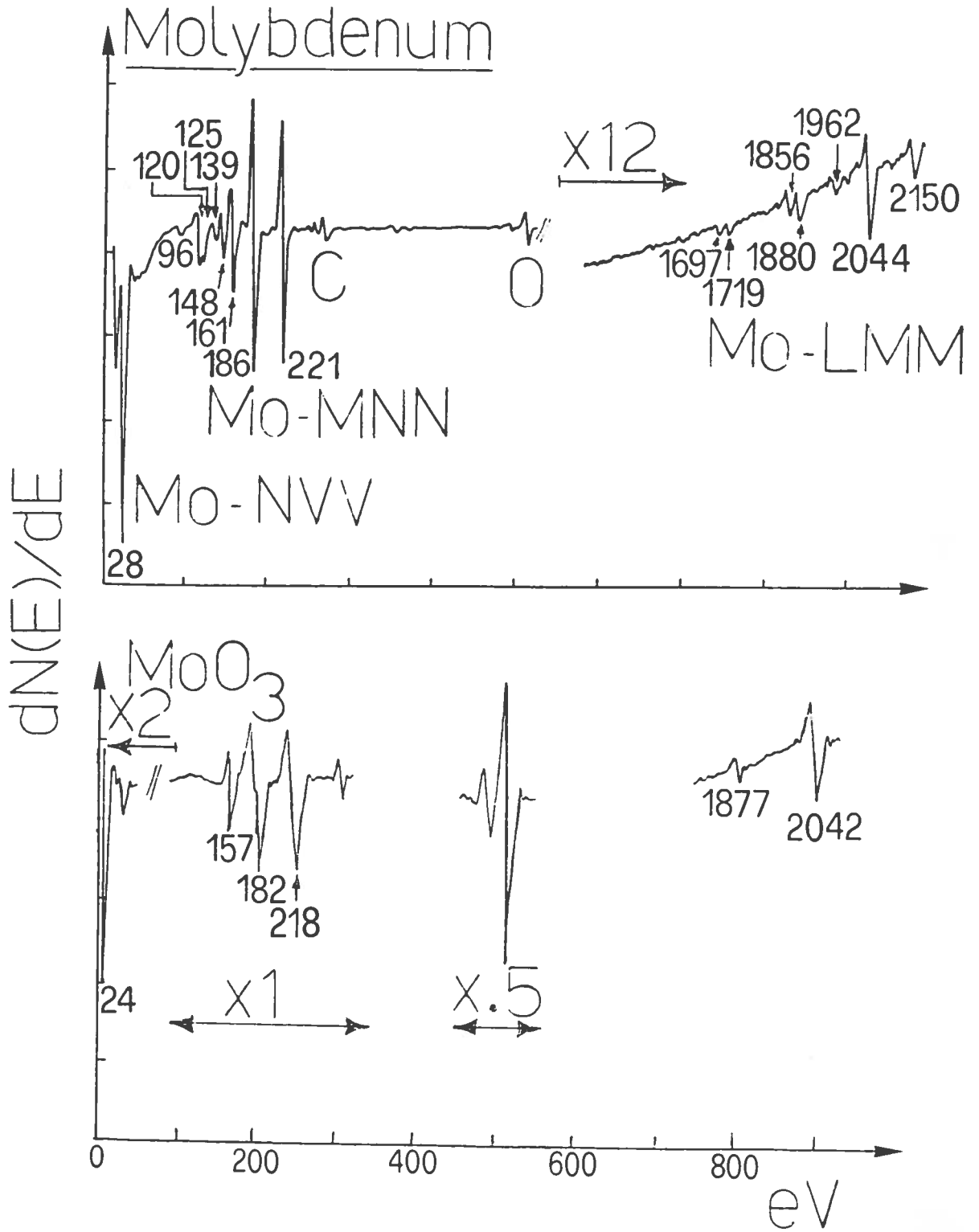


Fig.8

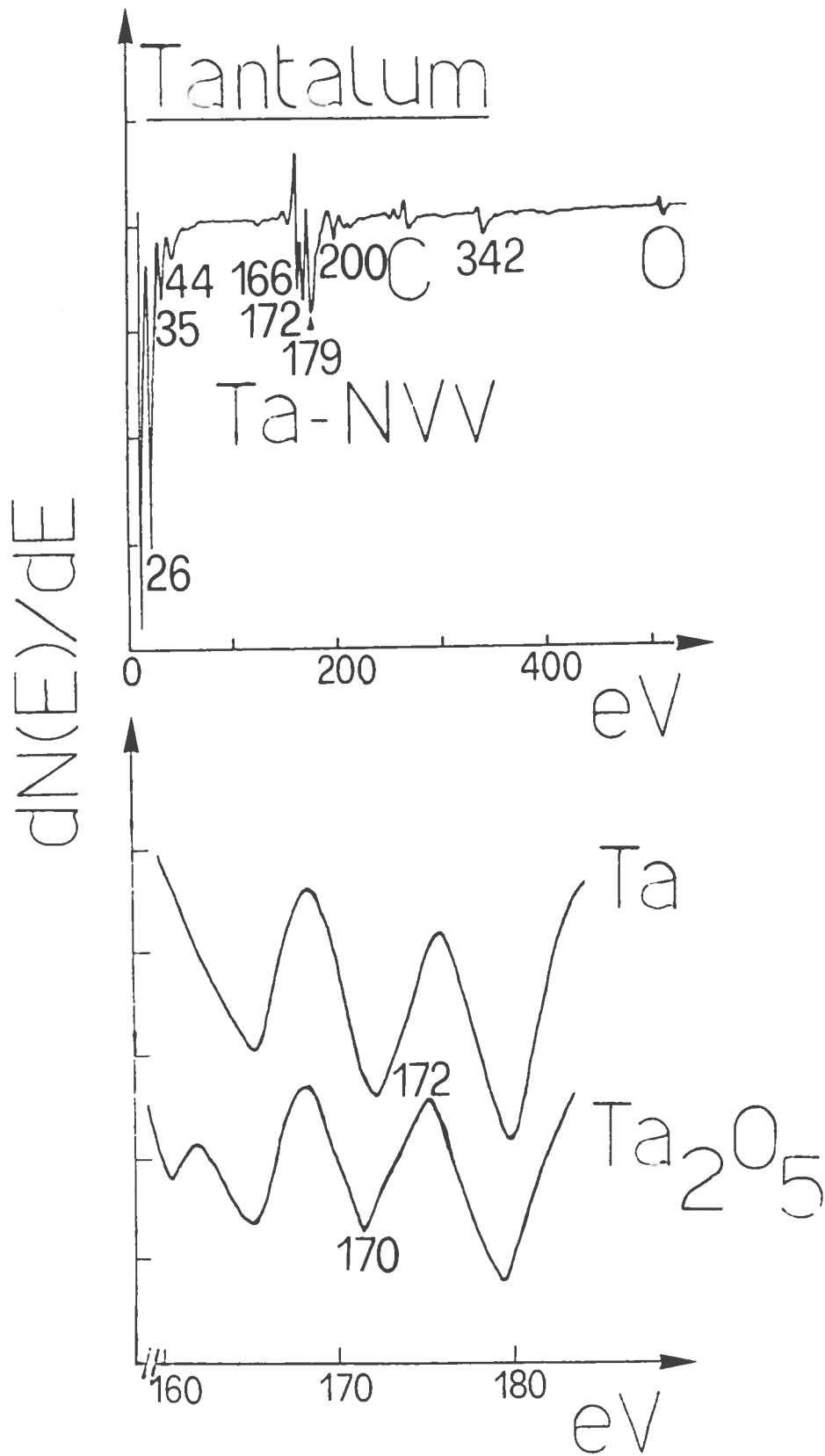


Fig.9

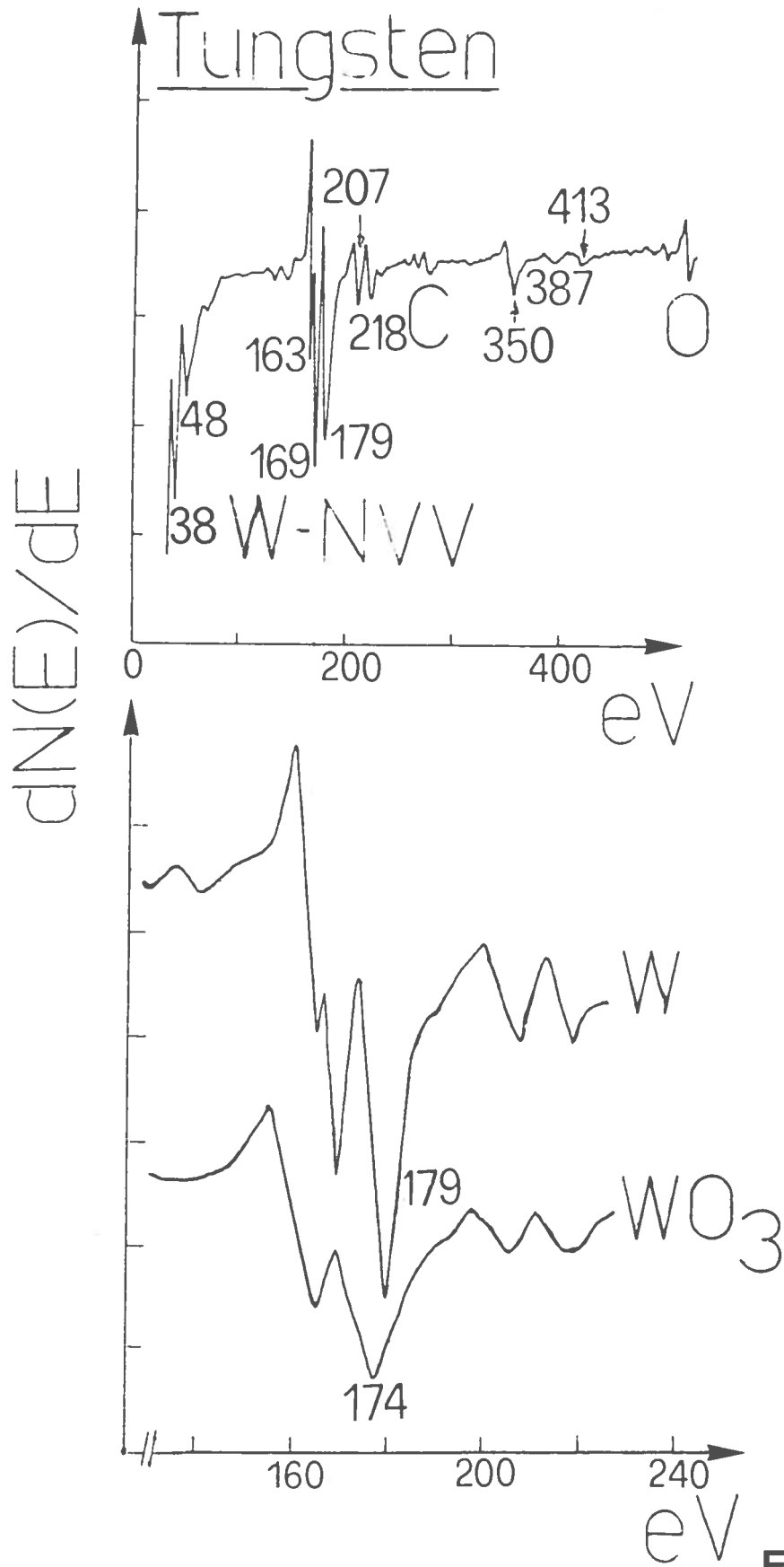


Fig.10

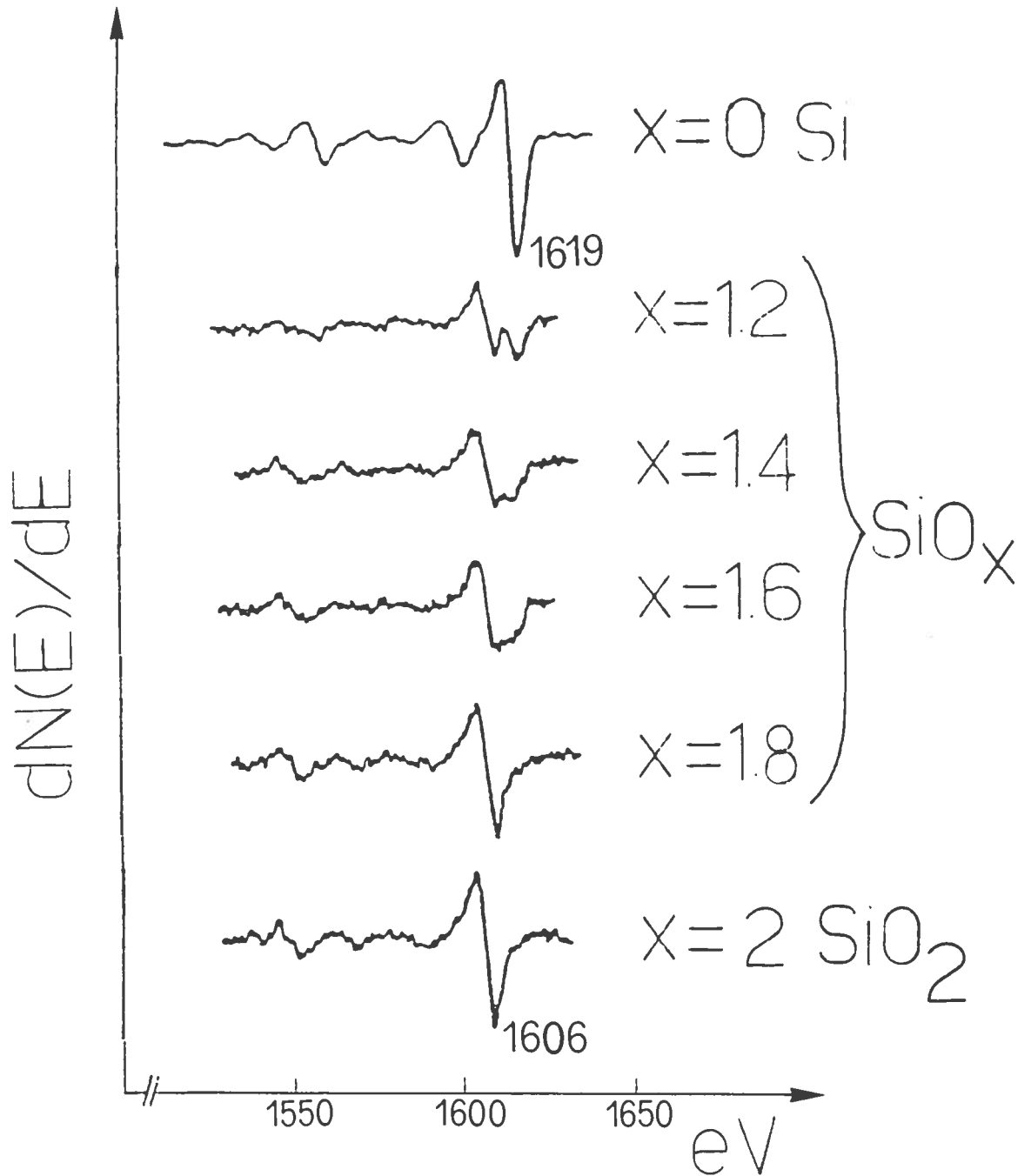


Fig. 11