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Optical Properties of CaWO_4 and CaMoO_4 Crystals in the
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R. Grasser¹⁾, E. Pitt¹⁾, A. Scharmann¹⁾, and G. Zimmerer²⁾

The reflection spectra of CaWO_4 and CaMoO_4 single crystals were measured in the region between 4 and 25 eV. The measurements were performed using the electron synchrotron DESY as a light source. Both crystals show very similar spectral features. A relatively sharp, well separated low energy peak is accompanied on the high energy side by two groups of maxima, each group containing three broad main reflection bands which strongly overlap. Besides this, a less pronounced structure is observed over the whole spectral region. The experimental results are discussed in terms of semi-empirical MO calculations of the anionic transition metal oxo complexes.

Die Reflexionsspektren von CaWO_4 - und CaMoO_4 -Einkristallen wurden zwischen 4 und 25 eV gemessen. Das Elektronensynchrotron DESY diente als Lichtquelle. Die Spektren der beiden Kristalle sind sehr ähnlich. Ein relativ scharfer, wohl getrennter, niederenergetischer Peak wird zu kürzeren Wellenlängen hin jeweils von zwei Bandengruppen gefolgt, die im wesentlichen aus drei sich stark überlappenden Maxima aufgebaut sind. Daneben ist über den ganzen Spektralbereich eine weniger ausgeprägte Struktur zu beobachten. Die experimentellen Ergebnisse werden mit Hilfe semiempirischer MO-Berechnungen der Anionenkomplexe diskutiert.

I. Introduction

Calcium tungstate has been of practical interest for a long time because of its attractive luminescence properties. During the last years strong attention has been focused on CaWO_4 , because it provides one of the best available solid state laser materials, being the only one to operate continuously at room temperature. This kind of application has stimulated a large number of investigations on impurity states in CaWO_4 and CaMoO_4 (1). Much less work has been done concerning the nature of the absorption and emission states of pure crystals.

The optical response of CaWO_4 and CaMoO_4 has been investigated throughout the visible and near ultraviolet on the long wavelength side of the absorption edge below about 5 eV (250 nm). While older measurements on these phosphors have been performed on powdered samples (2), recent studies have been done on single crystals (3,4) Walter and Butler (5) have measured excitation spectra of CaWO_4 powder samples in the 4.3 - 7.4 eV region. The authors converted the excitation curves into relative absorption spectra. Then the derived absorption spectrum of CaWO_4 has been resolved into Gaussian functions.

Further attempts to establish the absorption features beyond the bulk crystal transmission limit were by means of reflection techniques. Gurvich et al. (6) were able to investigate the reflection spectrum of a CaWO_4 crystal as far as 14 eV. At about 14 eV is the limit of useful emission from hydrogen discharge light sources.

Since the early measurements of Kröger and coworkers (2), electronic states of the WO_4^{2-} and MoO_4^{2-} transition metal oxo complexes have been regarded as important in the optical absorption and emission spectra of these oxygen-dominated phosphors at low energy. Yet, up to the present day there is no useful theoretical approach to a successful interpretation of the optical properties of these materials. The results of band theory are not applied to tungstates and molybdates. The lack of

theoretical band calculations is due to the fact that these solids have a high number of atoms in the unit cell. Electron energy diagrams of WO_4^{2-} and MoO_4^{2-} complexes derived with semiempirical molecular orbital methods are the only available theoretical basis (5,7,8).

The present paper reports the first measurements of highly resolved reflectance spectra of CaWO_4 and CaMoO_4 single crystals in the region 4 to 25 eV. The electron synchrotron DESY is used as a light source. The vacuum ultraviolet extinction of these solids should be mainly due to the excitation of valence shell electrons of the anionic complexes. Additional band processes may contribute to photoabsorption. The experimental data are analyzed in terms of molecularlike excitonic excitations.

2. Experimental

The calcium tungstate and calcium molybdate crystals used in this work were grown by the Czochralski technique of pulling from the melt. Both samples were annealed at 1000°C in air. The crystals were colourless and showed a negligible absorption in the visible. The transmission limit of the CaWO_4 crystal was measured at 4.6 eV, that of the CaMoO_4 crystal at 3.9 eV. The CaWO_4 specimen was a ultrahigh pure and perfect crystal.

The crystals (1 mm thick) were mechanically polished by means of a diamond paste of a 3 μm grain size and afterwards cleaned with absolute alcohol.

The reflection measurements were performed using the Deutsches Elektronen-Synchrotron, DESY, Hamburg, as light source. The properties of synchrotron radiation are described in Ref. 9. The experimental set up used in this experiment is shown in Fig. 1. The nearly parallel synchrotron radiation beam is monochromatized by a near normal incidence monochromator (10). A grating with 600 L/mm (Al + MgF_2 coated, blazed at 1200 \AA) is used for the low energy part of the spectra. For the high energy

part of the spectra a 1200 L/mm grating (Au coated, blazed at 600 Å) is used. The monochromatized light is focused onto the crystal by a toroidal mirror. The crystal is mounted onto a cryostat in a UHV sample chamber ($p < 10^{-8}$ Torr). A reference monitor converts part of the incident light from the vacuum ultraviolet to the visible by sodium salicylate. The converted light is detected by a photomultiplier. The reference signal measured in this way is proportional to the intensity of the incident light. The reflected light is also converted by sodium salicylate. Dividing the reflection signal by the reference signal yields the reflection spectrum in relative units.

Additionally, part of the reflection curves are measured without the phosphor using an open magnetic multiplier. In this case the reflected as well as the incident light are measured separately by rotating the multiplier around the sample and lifting the sample out of the beam. Dividing the reflected intensity by the incident intensity yields the reflectivity. The reflection spectra obtained with both methods agree well.

The measurements were performed at 300 and 80 K. The crystals were not aligned in relation to the polarization direction of the highly polarized synchrotron radiation.

3. Experimental Results

The reflection spectra of the CaWO_4 crystal at room temperature (RT) and at the temperature of liquid nitrogen (LNT) are shown in Fig. 2. The curves of Fig. 3 represent the reflection spectrum of the CaMoO_4 crystal at room temperature. The uncertainties of the reflectivity values are within 3%, those of the energy values within 1%.

At the low energy part of the CaWO_4 spectrum, that is below about 5 eV, the total measured reflectance may include contributions not only from the front surface, but also from the back surface of the crystal and from the surface of the sample mount immediately

behind the probe. These contributions have not been removed, so that no extrapolation to longer wavelengths is possible.

The reflection spectra give a good indication of the main electronic transitions occurring. A more basic parameter is the imaginary part of the complex dielectric response function. But no Kramers-Kronig-analysis is performed because the integration requires knowledge of the whole reflection spectrum, which, in our case, it is very poor in the near ultraviolet.

The reflection spectra of CaWO_4 and CaMoO_4 at RT show very similar features. Respectively, a first relatively sharp, well separated peak at low energy is accompanied by two groups of bands, each group containing three broad main reflection maxima which strongly overlap. The weak reflection peaks from about 15 eV to 25 eV are only poorly resolved from the continuous background. The energy values of the strong main peaks are summarized in Table 1.

Table 1

Position of the main peaks in eV in the reflection spectra of the valence region of CaMoO_4 and CaWO_4 .

Peak number	CaMoO_4	CaWO_4
1	5.0	5.9
2	7.5	7.6
3	8.4	8.3
4	9.2	9.4
5	10.3	11.7
6	11.7	12.3
7	13.4	14.6

The first well isolated peak of CaWO_4 shows a considerable blue shift relative to the corresponding maximum of CaMoO_4 . The same holds for the high energy peaks 5,6,7. Absorption and emission measurements in the visible and near ultraviolet also reflect this spectral behaviour (2,4). The peaks 2,3, and 4 of the two different crystals exhibit a surprising conformity with regard to the peak positions. In these parts of the spectra, however, the ratios of the peak intensities strongly differ between CaWO_4 and CaMoO_4 . While in calcium tungstate peak 3 is the most intensive maximum of this group and peak 2 is only present as a shoulder, peak 2 is the strongest maximum in the case of calcium molybdate and peak 4 a weak shoulder. On the other hand, the oscillator strength of CaMoO_4 is stronger than that of CaWO_4 in this spectral region. Peak 1 of CaWO_4 is more intensive than the corresponding maximum of CaMoO_4 .

Curve b of Fig. 2 presents the reflection spectrum of CaWO_4 at LNT. There are only insignificant deviations from the spectrum measured at RT. At LNT the reflectivity of peak 1 shows a small increase, that of peaks 5 and 6 a small decrease. The peak position of the well separated maximum 1 is independent of temperature within the accuracy of these measurements. The observed temperature shift of the positions of some higher energy peaks may be due to the change of the band widths as a function of temperature.

The reflection data presented in this report partly confirm the spectral features seen by Gurvich et al. (6). These authors have only observed the peaks 1,4,5, and 6 (after the peak notation used in this paper) at about the same energy positions. The maxima 2 and 3 are absent the reflection spectra. Gurvich et al.'s data, which are the only other comparative reflectance measurements up to 14 eV, seem rather questionable. The lack of peaks 2 and 3 in their spectrum may be the consequence of the used conventional light source.

4. Discussion

The absolute lack of any theoretical band calculation of CaWO_4 and CaMoO_4 strongly limits the possibilities of a more quantitative interpretation of the measured reflection spectra. Recent experimental attempts to establish the width of the band gap of CaWO_4 by means of photoconductivity measurements have been negative up to a 6.2 eV quantum energy (11). Under the same aspect Gurvich et al. have measured the phosphorescence excitation spectrum of CaWO_4 (6). They have observed phosphorescence at photon energies exceeding 6 eV. From this onset and from the decay characteristics of phosphorescence and the additional assumption that the necessary migration of charge carriers to the trapping sites takes place via the conduction band, the authors suggest that interband transitions occur at photon energies $E \geq 6,5$ eV. Besides these not very convincing details, there are no further informations about crystal states (band states and exciton states) in CaWO_4 and CaMoO_4 .

Somewhat more work has been done on the electronic states of the WO_4^{2-} and MoO_4^{2-} anions. These transition metal oxo complexes should play a significant and distinct role in the optical behaviour of the two crystals. According to published absorption spectra of aqueous solutions of the radicals WO_4^{2-} and MoO_4^{2-} the tungstate $5d^0$ system displays a band at 6.2 eV. The molybdate $4d^0$ system has the corresponding band at 5.5 eV with an oscillator strength $f = 0.106$. The authors have assigned these bands as the first allowed ligand \rightarrow metal electron transfer bands (12,13). The energies of these electronic transitions in MoO_4^{2-} and WO_4^{2-} as calculated with the excited states scheme of Gray's self-consistent charge and configuration molecular orbital (SCCC-MO) method are estimated to 5.9 and 6.4 eV, respectively (8). The calculated energies are in satisfactory agreement with experiment.

The semiempirical molecular orbital approaches used in this field are mostly of the one-electron Hückel or extended

Hückel type. In the self-consistent charge method allowance is given for dependence of the parameters on the degree of orbital occupancy. It is now assumed, however, that the results of such calculations have only a qualitative meaning. So Dahl and Ballhausen show for the MnO_4^- oxyanion that the calculated molecular orbital energy level diagrams strongly depend on the used MO approach concerning level sequence and orbital energies (14). In view of this background an attempt to assign the measured reflection bands to distinct electronic transitions in CaWO_4 and CaMoO_4 can only be a matter of trial and error.

CaWO_4 and CaMoO_4 both crystallize in the scheelite structure. The crystals can be regarded as ordered arrays of WO_4^{2-} or MoO_4^{2-} radicals ionically bound to Ca^{2+} cations. The solids contain the polyatomic anions as discrete complexes, where the tetrahedral tungstate and molybdate groups are part of the crystal unit cell. These structural properties of CaWO_4 and CaMoO_4 justify a molecular model as a basis for the interpretation of the optical behaviour of the investigated solids in the 4 - 25 eV energy region. It should be possible to assign the measured reflection bands in the valence region to the anions and to use MO calculations for the isolated oxyanions, with the above mentioned limitations in mind. A molecular rather than a band model is further supported by the observation that a change of the cations has only a minor influence on the luminescence of tungstate and molybdate phosphors (1,2).

The geometries of the WO_4^{2-} and MoO_4^{2-} complexes in the crystals are not completely regular. The oxyanions are distorted from T_d to the site group symmetry D_{2d} by a compression along the c axis. Crystal structures reveal the following interatomic distances and bond angles for CaWO_4 (15) and CaMoO_4 (16):

$\text{W-O} = 1.788 \text{ \AA}$	$\text{Mo-O} = 1.757 \text{ \AA}$
$\alpha = 113^\circ 27'$	$\alpha = 115^\circ 0'$
$\gamma = 107^\circ 56'$	$\gamma = 106^\circ 46'$

The measured $\text{O}_n\text{-X-O}_m$ angle deviations ($X = \text{W, Mo}$) from the ideal 109° tetrahedral angle are smaller for the WO_4^{2-} anion as compared

to the MoO_4^{2-} complex. The geometrical data indicate that the departure from pure tetrahedral symmetry is not very large. Thus we might expect that T_d symmetry should still dominate the reflection spectra.

Sleight has measured the cell dimensions of molybdates and tungstates (17). He concludes from electrostatic arguments that the MoO_4^{2-} group should be more covalent than the WO_4^{2-} group.

The transition metals Mo and W belonging to the same group of the periodic system (IV B) have the same oxidation state in the two oxyanions of interest (oxidation number VI). However, MoO_4^{2-} is a 4d complex, WO_4^{2-} a 5d complex. It is a general result of ligandfield theory that the first allowed charge transfer band shifts to higher energy proceeding from first-row to third-row in an analogous series of transition metal complexes. This behaviour is exactly verified in our measurements.

Various authors have discussed the form of molecular orbitals (MO's) for a tetrahedral oxo complex (3,14,18). For MO calculations a core is defined consisting of the metal and ligand nuclei, the 1s electrons of the ligands, and all electrons in the highest "rare gas core" involved in the central metal ion. The core electrons are assumed to reside in the same atomic orbitals as in the free ions. The remaining electrons in the complex are considered as valence electrons. The 2s and 2p orbitals of the oxygen ligands are used along with the metal ion nd, (n+1)s, and (n+1)p orbitals (Mo: n=4; W: n=5) to construct MO's with T_d symmetry. The bonding MO's primarily involve the ligand orbitals, and they are classified as to type σ and π .

Fig.4a shows the MO energy level diagram of the regular tetrahedral (T_d -symmetry) WO_4^{2-} complex, as calculated in (8).

Apart from orbital energies a similiar level scheme exists for MoO_4^{2-} complexes except that in this case the orbital $3a_1$ is higher in energy than the $5t_2$ MO (8). As mentioned above, the level diagram of Fig.4a can serve as a basis for a mainly qualitative discussion of our reflection spectra, only.

It is considered that the optical properties of CaWO_4 and CaMoO_4 in the most interesting 4 to 15 eV region is due to electronic transitions of charge transfer type between the fully occupied orbitals $1e$, $2t_2$, $2a_1$, $3t_2$, t_1 and the two empty orbitals $2e$ and $4t_2$ within the energetically well separated middle part of the level scheme. The ground state of the MoO_4^{2-} and WO_4^{2-} d^0 closed shell configurations is of symmetry 1A_1 , respectively. Only $^1A_1 \rightarrow ^1T_2$ transitions are allowed in tetrahedral symmetry. The selection rules for both electric and magnetic dipole transitions in T_d symmetry are given in Table 2.

Table 2

Electric and magnetic dipole selection rules

T_d	x, y, z	$L_{x, y, z}$
A_1	T_2	T_1
A_2	T_1	T_2
E	$T_1 T_2$	$T_1 T_2$
T_1	$A_2^E T_1 T_2$	$A_1^E T_1 T_2$
T_2	$A_1^E T_1 T_2$	$A_2^E T_1 T_2$

The representations of the point group T_d are given in the first column. The representations which are able to combine

with them are presented in the succeeding columns under x, y, z for electric dipole and $L_{x, y, z}$ for magnetic dipole transitions. The excitation can produce a singlet and a triplet system of excited states.

In the case of MoO_4^{2-} and WO_4^{2-} only the first transition is calculated with the excited states scheme of the SCCC - MO method which is assigned to an one-electron $t_1 - 2e$ transition (8). The calculated transition energies are:

WO_4^{2-}	$t_1 \rightarrow 2e$	6.4 eV
MoO_4^{2-}	$t_1 \rightarrow 2e$	5.9 eV

The reflection spectra of CaWO_4 and CaMoO_4 according to our measurements show the first main peaks at 5.9 (6.2) and 5.0 (5.5) eV, respectively. The values in paranthesis are the corresponding transition energies of the oxyanions as measured in aqueous solution (12). The "solid state values" are clearly smaller than the "aq. solution values", and the experimental again smaller than the calculated values. Because of the satisfactory agreement of all these values the low energy reflection peaks of CaWO_4 and CaMoO_4 at 5.9 and 5.0 eV are assigned to the orbitally allowed first electron transfer transition ${}^1A_1 \rightarrow {}^1T_2$ in the oxyanions. The electronic transitions $t_1 \rightarrow 2e$ are of $\pi \rightarrow \pi^*$ character since t_1 is a non-bonding molecular orbital built from oxygen $2p_\pi$ atomic orbitals and the $2e$ MO consists mainly of $d(\pi)$ metal orbitals. The assignment is further confirmed by oxygen-17 nuclear magnetic resonance measurements on these compounds. A linear relationship is observed between the chemical shifts for these closed shell oxyanions and their lowest energy electronic transitions as obtained from optical spectroscopy (19).

Kebabcioglu and Müller (8) report that it is not possible to assign the transitions to higher excited states with the theoretical approach of the SCCC - MO method. The excitation energies cannot be calculated from the orbital energies as given in Fig.4a. They differ from the orbital energy difference by electron-electron interaction terms.

The transition of next highest reflectivity and energy is expected to involve the t_1 orbital and the σ -antibonding MO $4t_2$. The $4t_2$ molecular orbital contains the $d(\sigma)$ orbitals of the central transition metal ion. The reflectivity peaks at 7.5 eV in CaMoO_4 and 8.3 eV in CaWO_4 are assigned to the orbitally allowed transition $t_1 \rightarrow 4t_2$ (${}^1A_1 \rightarrow {}^1T_2$) in the corresponding oxyanions. The weak shoulder at the low energy side of the 8.3 eV reflectivity peak of CaWO_4 is assigned to the spin allowed but orbitally forbidden $t_1 \rightarrow 4t_2$ electronic transition ${}^1A_1 \rightarrow {}^1T_1$. These assignments seem reasonable in respect to the energy differences of the two orbitally allowed transitions $t_1 \rightarrow 2e$ and $t_1 \rightarrow 4t_2$ of CaWO_4 and CaMoO_4 . The $2e$ and $4t_2$ roughly correspond to the orbitals e and t_2 of crystal-field theory. Thus the energy differences of the $t_1 \rightarrow 2e$ and $t_1 \rightarrow 4t_2$ transitions have to be related to the ligand-field splitting of $2e$ and $4t_2$. The splitting parameter of about 2.5 eV is consistent with the value one should expect from an extrapolation of the splitting factor of the analogous 3d complex CrO_4^{2-} (7).

The transitions of next higher energy are expected to correlate with the (π, σ) $3t_2$ orbital. The reflection peaks at 8.4 eV for CaMoO_4 and 9.4 eV for CaWO_4 are assigned to the allowed electronic transitions $3t_2 \rightarrow 4t_2$ (${}^1A_1 \rightarrow {}^1T_2$). The energy splitting of the orbitally and spin allowed transitions $t_1 \rightarrow 4t_2$ and $3t_2 \rightarrow 4t_2$ is related to the interaction of the oxygen levels. The splitting energy of about 1 eV is reasonable compared to other transition metal oxo complexes.

The last two pronounced reflectivity maxima at 10.3 and 11.7 eV in the spectrum of CaMoO_4 , 11.7 and 12.3 eV in the spectrum of CaWO_4 we assign with the spin allowed and orbitally forbidden $2t_2 \rightarrow 2e$ (${}^1A_1 \rightarrow {}^1T_1$) low energy peak and the allowed $2t_2 \rightarrow 2e$ (${}^1A_1 \rightarrow {}^1T_2$) high energy peak electronic transitions. This assignment seems reasonable on account of the relatively weak intensities of these reflectivity peaks. The transitions $2t_2 \rightarrow 2e$ are of character $(\sigma, \pi) \rightarrow \pi^*$ which should be weak. Electronic transitions $2t_2 \rightarrow 4t_2$ of the $(\sigma, \pi) \rightarrow \sigma^*$ type are not of experimental evidence since due to Mulliken's principle nearly all very

strong bands are caused by transitions between σ -bonding and σ -antibonding orbitals. If the assignment $2t_2 \rightarrow 4t_2$ would be true, the last two weak main peaks of the spectra should show substantial higher reflectivity values compared to the lowest energy peaks since the latter are $\pi \rightarrow \pi^*$ transitions (the part of π -character in $(\pi, \sigma) 3t_2$ is about 2/3). The results are summarized in Table 3.

Table 3: Assignment of the measured reflectivity peaks with electronic transitions within the oxyanions MoO_4^{2-} and WO_4^{2-} .

Transition	MoO_4^{2-} (eV)	WO_4^{2-} (eV)
$t_1 \rightarrow 2e$ (${}^1A_1 \rightarrow {}^1T_2$)	5.0	5.9
$t_1 \rightarrow 4t_2$ (${}^1A_1 \rightarrow {}^1T_1$)		7.6
$t_1 \rightarrow 4t_2$ (${}^1A_1 \rightarrow {}^1T_2$)	7.5	8.3
$3t_2 \rightarrow 4t_2$ (${}^1A_1 \rightarrow {}^1T_2$)	8.4	9.4
$2t_2 \rightarrow 2e$ (${}^1A_1 \rightarrow {}^1T_1$)	10.3	11.7
$2t_2 \rightarrow 2e$ (${}^1A_1 \rightarrow {}^1T_2$)	11.7	12.3

The measured reflectivity intensities of our spectra must be considered with some caution. Up today we have not measured a possible influence of the polishing procedure on the spectra. We feel that such an influence should be negligible since CaWO_4 and CaMoO_4 are very stable compounds. A more serious effect on the band intensities may be caused by the reflectivity representation itself. A more exact representation is a plot of the imaginary part of the complex dielectric response as function of photon energy (20).

The very weak reflectivity peaks between about 15 and 25 eV cannot be discussed at the present stage. The same holds for the influence of D_{2d} perturbation (Fig. 14b) and spin orbit coupling (5) which should introduce additional structures in the low energy part of the spectra. Measurements which make use of the polarization properties of synchrotron radiation shall give here further informations.

The data of our reflection spectra do not allow to speculate definitely about band properties of CaWO_4 and CaMoO_4 . The molecular-like excitations in the oxyanions, as discussed above, have to be viewed in the solid compounds as Frenkel excitons in the sense that, because of crystal periodicity, the excitation must be shared by all the atoms. The $4t_2$ molecular orbitals include σ as well as π ligand orbitals together with metal nd and $(n + 1)p$ orbitals. Electrons excited in these $4t_2$ orbitals may be still bound, but enough delocalized to show conduction band effects to some extent. A strong overlap should be expected between $(n + 1)s$ and $(n + 1)p$ orbitals of the nd transition metals ions on neighbouring sites. This means that the $3a_1$ and $5t_2$ orbitals will broaden into conduction bands of the crystals.

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Figure Captions

- Fig. 1. Experimental set-up for the reflectance measurements.
- Fig. 2 Reflectivity of the CaWO_4 crystal in arbitrary units as a function of photon energy a) at room temperature, b) at the temperature of liquid nitrogen.
- Fig. 3. Reflectivity of the CaMoO_4 crystal in arbitrary units as a function of photon energy at room temperature.
- Fig. 4. Molecular-orbital level diagram of the tungstate anion a) for T_d symmetry, b) for D_{2d} symmetry. The values for the orbital energies in T_d symmetry are taken from (8). The diagram b shows the level splitting in D_{2d} symmetry only qualitatively.

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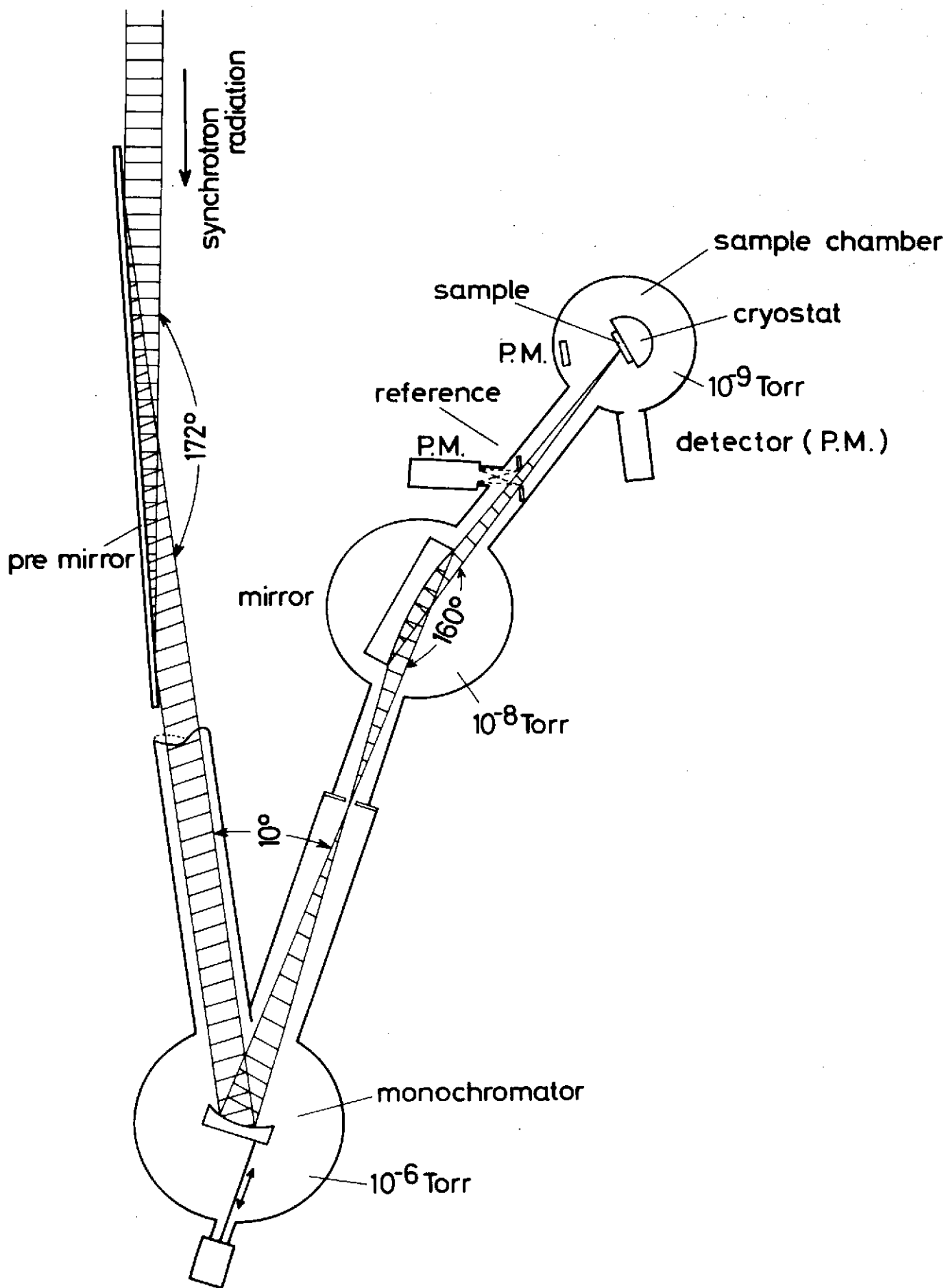
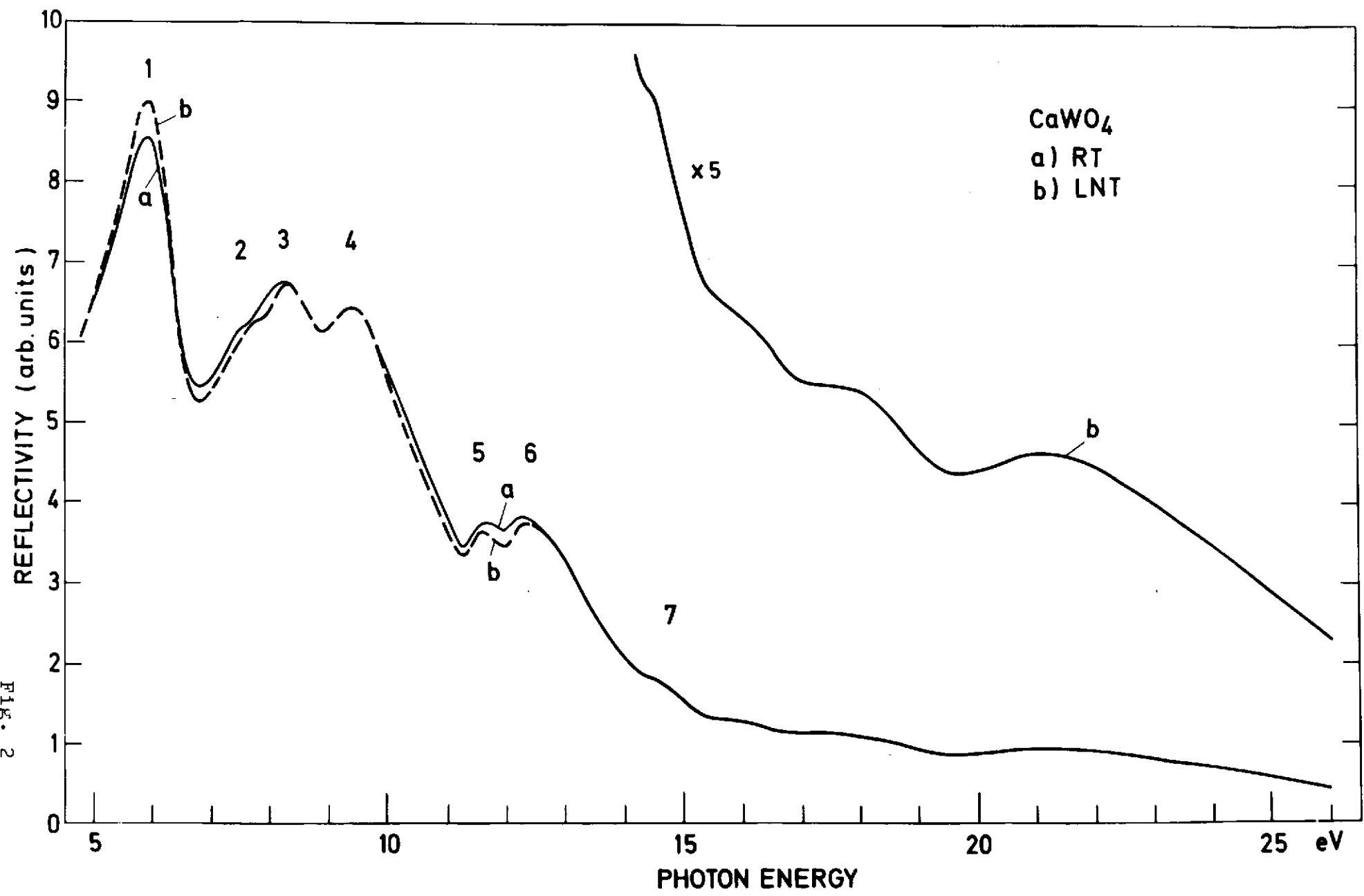
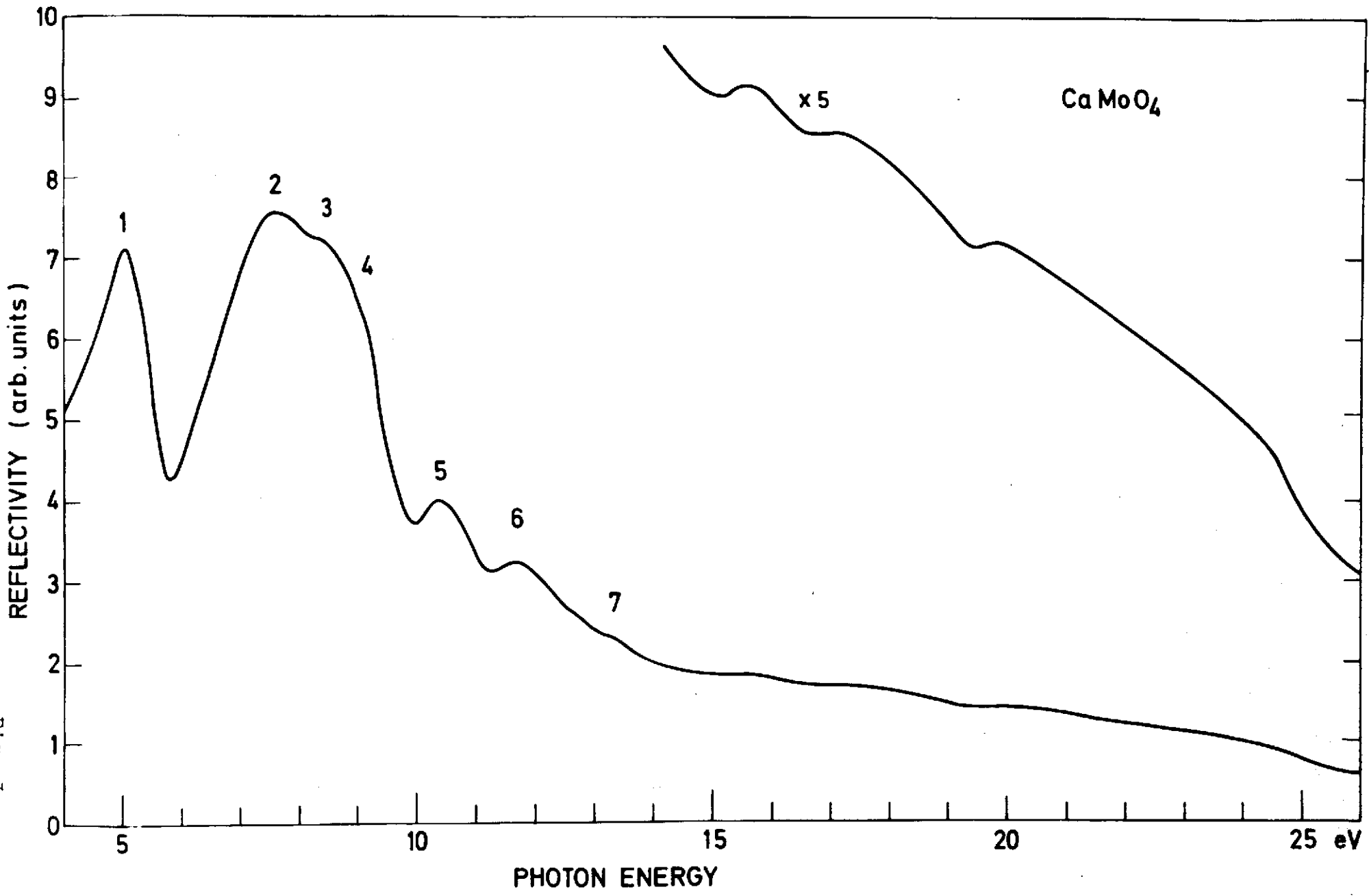
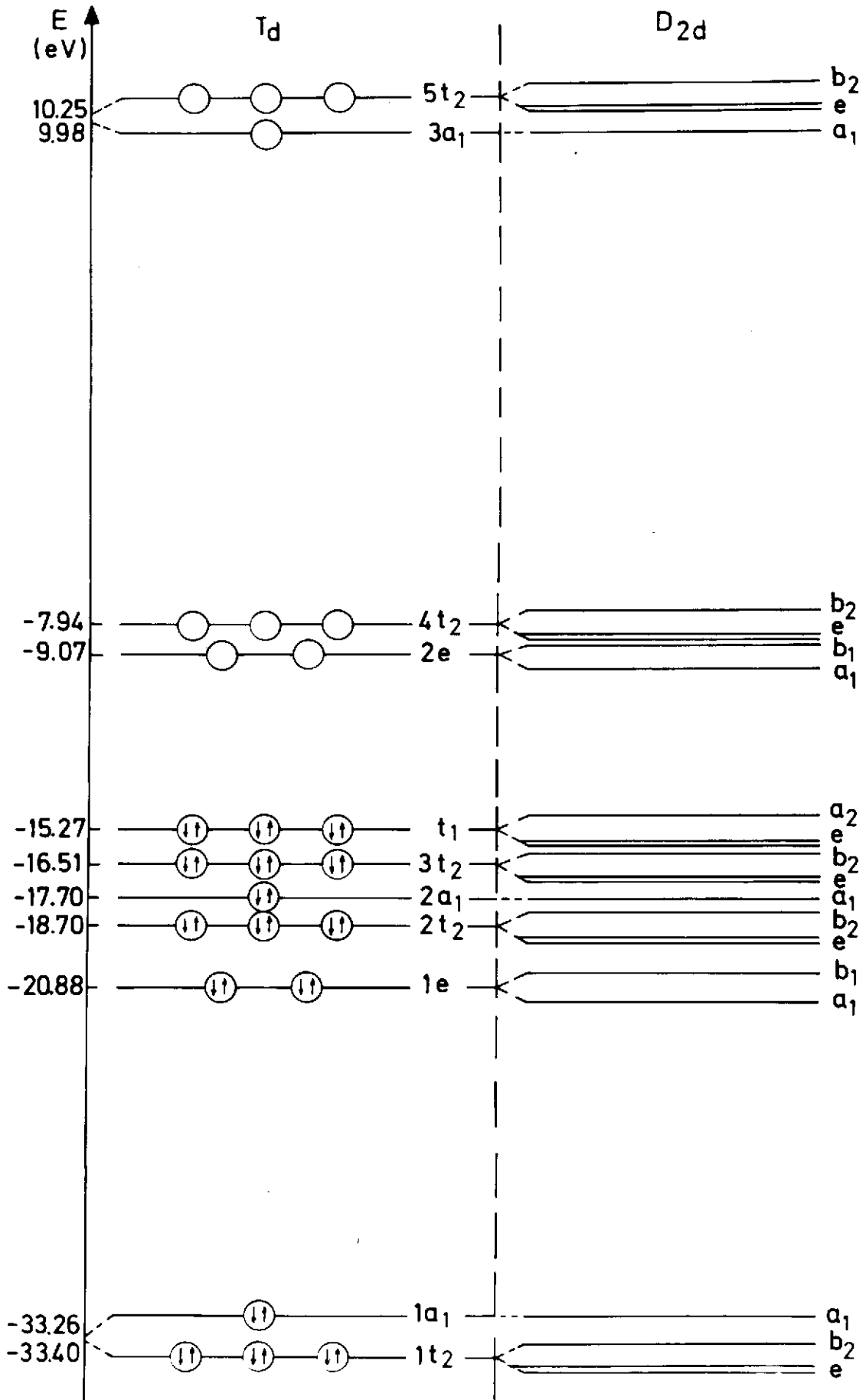
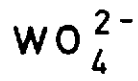


Fig. 1

FIG. 2







a

b