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## Excitation of the Cs-5p Core Level in Cesium Halides at 30 K

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*The excitation of the Cs-5p core level in Cs-halides which starts at about 13 eV was studied by measuring the reflection spectra of evaporated films between 12.5 eV and 26 eV at room temperature and at 30 K. Synchrotron radiation was used as a light source. In comparison to the spectra at room temperature new remarkable fine structure was found at 30 K. The very complex spectra are discussed with regard to band calculations including excitons associated with critical points. In a complementary view the spectra are compared with transitions of the free Cs<sup>+</sup> ion. A sideband at the high energy part of the most prominent exciton was observed for every Cs halide. It is presumably caused by exciton-phonon interaction.*

## 1. Introduction

In comparison to other alkali halides the Cesium halides have an electronic level extremely close below the halogen-type valence band. This level is formed by the weakly bound outer 5p electrons of the positive Cesium ion. It can already be excited by photons with energies exceeding 13 eV [1-4]. Recently the excitation of the  $\text{Cs}^+5\text{p}$ -level was independently studied for different Cs halides by measuring reflection spectra [1, 2] and absorption spectra [3, 4] with higher resolution and, partly, at lower temperature than before. In these experiments many new interesting features were observed in comparison to older optical absorption work [5] or electron energy loss measurements [6]. However, some apparent inconsistencies still remained between different authors' results, e.g. between the absorption results in ref. [3] and [4]. Furthermore, the attempted interpretation of the spectra did not seem to be unambiguous.

The great variety of lines recently found in the spectra was discussed with the help of two complementary approaches: The conventional approach was to start with band calculations and excitons associated with critical points [1-4]. Since there were only band calculations for CsF [7] and CsI [8, 9] and no calculations of the density of states, the interpretation following this line remained unsatisfactory and, in many cases, highly speculative. For instance, an extra large crystal field splitting of the  $\text{Cs}^+5\text{p}$  level at the point X or M in the Brillouin zone as well as exchange effects had to be assumed in order to explain the complex spectra.

On the other hand, in the second approach the spectra were compared with the excitation energies of the free Cs ion [1]. This yielded results not worse than those obtained by the first approach. The second approach is surprisingly

simple. It also explains, in a straightforward manner, the existence of sharp line profiles. Apparently, it has to be improved by including crystal field effects due to neighbouring atoms. Both approaches have also recently been used to interpret the excitation spectra of the  $\text{Rb}^+4p$  level in Rb halides starting at 16 eV [10, 11].

For better comprehension of the  $\text{Cs}^+5p$  excitation and in order to confine too wide theoretical speculation it is necessary to carry out optical measurements with as high a resolution as possible and at as low a temperature as possible over wide energy ranges. Studies of the temperature dependence are also useful. - In this work the first reflection measurements at a temperature down to 30 K with a wavelength resolution of  $2 \text{ \AA}$  (i.e.  $\sim 30 \text{ meV}$  at 13 eV) are reported for all Cs halides in the energy range 12 to 26 eV. Reflection spectroscopy was preferred because this technique is believed to be more sensitive to fine structure than absorption. Furthermore, no difficulties arise due to the transparency of the substrate.

## 2. Experimental Procedure

Synchrotron radiation from the Deutsches Elektronen-Synchrotron DESY was used as a light source [12]. A normal incidence monochromator [13] provided light in the wavelength range between 450 Å and 1000 Å (26 eV and 12.5 eV). The resolution was 2 Å (i.e. 0.03 eV at 13.3 eV). The absolute accuracy in determining wavelengths was  $\pm 1$  Å.

The experimental set-up for the reflection measurements is shown in Fig. 1. The monochromatic light was reflected from the sample at 15° angle of incidence. It was detected by an open magnetic multiplier. In contrast to the relative spectral shape the absolute value of the reflectance was not determined with high accuracy, since the incident and reflected light were not measured simultaneously.

The Cs halides were evaporated in situ at room temperature on a polished stainless steel plate which was coated with gold. The plate was mounted on the outer side of the cooled block of the cryostat. In order to reduce contamination a cooling shield surrounded the sample. The film thickness was above 1000 Å.

The cryostat assembly was mounted into an ultra high vacuum chamber where a pressure in the  $10^{-9}$  Torr range was sustained before cooling and during measurement. The temperature on the surface of the plate was simultaneously measured with an Fe-Au thermocouple and a calibrated germanium resistance thermometer. After cooling the cryostat with liquid He the sample reached a temperature of  $29 \pm 1$  K.

Contamination was negligible. After measuring for three hours, the reflectivity of the cooled sample was only about 10 % lower than at the beginning of the experiments; no significant changes were detected concerning the spectral structure.

### 3. Results and Comparison with previous Measurements

Figure 2 shows the reflection spectra of all Cs halides at the onset of the  $Cs^+5p$  excitation for room temperature (RT) and at 29 K between 12.5 and 17.5 eV. Figure 3 presents the spectra above 16.5 eV. The position of the peaks and shoulders are listed in Tables 1 and 2. The reflection spectra at room temperature and at 29 K were adjusted relative to each other so that the maxima of the highest peaks coincide and have the same value 1.0. The units in Fig. 3 follow this convention. The absolute values for the reflection maxima increase very strongly during cooling: for the predominant peak at about 13 eV we obtained intensity ratios  $R(29\text{ K})/R(\text{RT})=1.8, 1.5, 2.2, 2.5$  for CsF, CsCl, CsBr, and CsI respectively with an accuracy of about 10 %.

Figure 4 shows the main peak at about 13 eV in an extended energy scale. A sideband or at least a typical asymmetry at the high energy side was observed for all halides.

Spectra for samples evaporated and measured at 30 K were similar to those for samples evaporated and measured at RT. After the samples prepared at low temperature were heated up to RT and cooled again the sharp structures in the spectra reappeared. Smaller crystallites, presumably obtained by evaporation at low temperature, caused apparently more damping and the size of the crystallites was changes by heating.

As far as the energy position is concerned the absorption spectra of Saito and coworkers [3] generally agree fairly well with our reflection spectra (Figs. 5 and 6) in the region from 13 eV to 15.5 eV taking into account slight differences which are expected because of actual differences between absorption and reflection spectra. In that energy range our data, however, reveal more details

as, for instance, the sideband accompanying the main exciton. Furthermore, our data show, in general, a smaller 'background reflection', so that the excitation maxima emerge more clearly from the background. Above 15.5 eV the reflection spectra show much more detailed structure. Beyond 17.0 eV older absorption measurements taken at RT with a line source [5] exist. They show less structured spectra than those in Fig. 3.

The absorption measurements of Boursey and Roncin are claimed to be taken with a higher resolution ( $0.5 \text{ \AA}$ ) and at lower temperature (20 K) [4], but actually they do not show as many details in the case of CsI (Fig. 6) and CsBr. Boursey and Roncin have obtained very different peak positions and half-widths for CsCl (Fig. 5) which cannot be explained by lower temperatures because they are partly already present at 80 K.

Rubloff and coworkers [2] have measured reflection spectra of CsCl and CsBr crystals at 400, 300 and 90 K. As far as can be seen from the published figures they obtained results similar to ours. For both materials, however, we could resolve more details between 12.5 and 26.5 eV. Another point worth comparing is our larger increase of reflectance during cooling. Rubloff and coworkers obtained the reflectivity ratio  $R(90 \text{ K})/R(300 \text{ K})$  1.2 for CsCl and 1.3 for CsBr in the highest peak at about 13 eV. If we calculate  $R(29 \text{ K})/R(300 \text{ K})$  by multiplying the values of Rubloff et al. with those for  $R(29 \text{ K})/R(90 \text{ K})$  measured by us during cooling, we obtain 1.3 for CsCl and 1.5 for CsBr. These values are considerably smaller than our original ones (1.5 and 2.2).

The absolute reflectivity in the highest peak at about 13 eV given by Rubloff and coworkers (0.45 and 0.65 for CsCl and CsBr at 90 K) is extremely high in



comparison to reflectance values found for the first  $K^+3p$  and  $Rb^+4p$  excitations in other alkali halides. Although we did not intend to measure very accurate values, rough estimates never yielded reflectance values above 0.25 at the 13 eV peak (average values were about 0.1) for the Cs halide films.

#### 4. Discussion and Interpretation

The onset of transition from the  $\text{Cs}^+5p$  level, the first electronic level below the valence band, is indicated by the prominent sharp maxima at about 13 eV found in the reflection spectra of all Cs halides as shown in Fig. 2. The lowest lying transition for the free Cs ion is also located at 13.17 eV [14]. While the halogen ion is exchanged the excitation energies remain approximately unaffected, indicating that, from an atomic point of view, the transition is fairly localized at the Cs ion. Below 12 eV only transitions from the valence band occur. They have been systematically studied in absorption by Teegarden and Baldini [15] and others and will not be discussed here.

##### 4.1 Band structure and excitons

The spectrum of CsF which crystallizes in the rock salt (face centered cubic) structure looks characteristically different as compared to the spectra of the other Cs halides, which have simple cubic lattices (Fig. 2). According to the different crystal structure the hitherto available band structures for CsF and CsI are different (Figs. 7, 8). The  $\text{Cs}^+5p$  band has not been calculated but is presumably quite flat all over the Brillouin zone because it represents well localized states. Since no density of states or even  $\epsilon_2$ -calculations are available no attempt can be made to separate single particle effects (band to band transitions with matrix elements) and excitonic effects. Because the prominent lines of the spectra are fairly sharp with half-widths of about 0.2 eV we suggest that they are of excitonic nature rather than due to interband effects. The problem is, then, to attribute the exciton lines to critical points in the Brillouin zone to which they are coupled.

##### 4.1.1 CsF

In the case of CsF the strong peak  $A_1$  shifts markedly to higher energies by 0.14 eV when the temperature is lowered from room temperature to 29 K. The temperature

dependence and the small half-width ( $\sim 0.2$  eV at 29 K) suggest assigning  $A_1$ , the first strong excitation in the spectrum considered here, to a  $\Gamma_8 \rightarrow \Gamma_1$  excitonic transition [16, 17]. Its probable spin-orbit mate  $A_2$  showing the same temperature dependence as  $A_1$  is found at about 1.66 eV higher energy (at 29 K). The latter value is not far from the value 1.72 eV for the spin-orbit splitting of the ionization energies of the free  $\text{Cs}^+$  ion [14]. The next symmetry point where an exciton can be formed is  $X_3$ . The transition found at 17.74 eV (29 K) may be associated with such an exciton. It is separated from  $A_1$  by 4.71 eV. A value of 4.63 eV is obtained from band structure calculations [7]. In this picture, however, the very strong peak  $B_1$  together with its probable spin-orbit mate  $B_2$  and the small structure C between  $A_1$  and  $B_1$  remain unexplained. Even a transition at  $L_1$ , where no  $M_0$ -singularity is found, cannot account for  $B_1$  because the energy difference  $\Gamma_1 - L_1$  is far too large.

#### 4.1.2 CsCl, CsBr, CsI

The spectra of CsCl, CsBr and CsI (Fig. 2) differing markedly from those of CsF are characterized by three groups of excitations: the first at about 13 eV, the second at about 15 eV and the third between 16 and 17 eV. They are split at low temperature: the first in  $A_1$  and  $B_1$ , the second in  $A_2$  and  $B_2$ .  $A_1$  and  $A_2$  show only little temperature dependence in the case of CsCl and CsBr. They weakly shift to somewhat lower energies with decreasing temperatures in CsI.  $B_1$  and  $B_2$ , however, shift considerably to higher energies with lower temperatures. The splitting with temperature is between 0.2 and 0.3 eV, one of the strongest observed for alkali halides. The same temperature dependence of  $A_1$ ,  $A_2$  and  $B_1$ ,  $B_2$  respectively suggest that  $A_2$  is the spin-orbit mate of  $A_1$  and  $B_2$  that of  $B_1$ . Furthermore we obtained at 29 K for the distances  $A_1 - A_2$  ( $B_1 - B_2$ ) the values 1.72 (1.58), 1.58 (1.56), 1.63 (1.61) eV for CsCl, CsBr and CsI respectively which are very close to the spin-orbit splitting of the ionization energies of

the free  $\text{Cs}^+$  ion 1.72 eV [14]. For the simple cubic Cs halides band calculations were only published in the case of CsI [8, 9] (Fig. 8). CsI will, therefore, be discussed as representative for the whole group of simple cubic Cs halides. A correct assignment for the peaks in the CsI spectrum is very difficult, since  $\Gamma_1$ ,  $\Gamma_{12}$  and  $M_3$  lie energetically very close together. This is in contrast to many other alkali halides with fcc structure (cf. Fig. 7) where the bottom of the conduction band  $\Gamma_1$  is, energetically, much more separated from the next important point in the Brillouin zone,  $X_3$ , to which excitons are believed to be coupled. A clearly separated, so-called X-exciton is usually observed in the fcc case well above the  $\Gamma_1$  exciton.

Rössler's calculations [9] and those by Onodera in their revised form [8] (Fig. 8) suggest that the first prominent peak  $A_1$  is due to an exciton  $\Gamma_8^-$  (Cs 5p band)  $\rightarrow \Gamma_6^+$  ( $\Gamma_1$ ) (the bottom of the conduction band) having a spin-orbit partner  $A_2$ ,  $\Gamma_6^- \rightarrow \Gamma_6^+$  ( $\Gamma_1$ ). Then  $B_1$  and  $B_2$  may be assigned to the excitonic transitions  $\Gamma_8^- \rightarrow \Gamma_8^+$  ( $\Gamma_{12}$ ) and  $\Gamma_6^- \rightarrow \Gamma_8^+$  ( $\Gamma_{12}$ ). For the structure  $C_1$ ,  $D_1$ ,  $E_1$  between  $B_1$  and  $A_2$  one may assume excitons as being coupled to the low lying M points of the conduction band [8]. Saito and coworkers have assumed a considerable crystal-field splitting at the M point for the Cs5p core level [3]. They explained  $D_1$  and  $E_1$  as excitons from  $M_6^-$  and  $M_7^-$  (Cs 5p) to  $M_6^+$  ( $M_1$ ) or  $M_7^+$  ( $M_5$ ) with the spin-orbit mate  $C_2$  as  $M_6^-$  to  $M_6^+$  ( $M_1$ ) or  $M_7^+$  ( $M_5$ ). The crystal-field splitting  $M_6^- - M_7^-$  would be extremely large, about 0.5 eV. This value is even larger than the valence band splitting at M (about 0.43 eV) [8], although the wave functions of the core level are more localized. Large exchange effects [18] have to be assumed for this interpretation.

The following assignment can be attempted without invoking exchange contribution:  $C_1$ ,  $D_1$  and  $E_1$  are excitons from the Cs5p band to  $M_7^+$  ( $M_3$ ),  $M_6^+$  ( $M_1$ ), and

$M_7^+(M_5)$  in the conduction band, the first two having spin-orbit mates in the long shoulder  $C_2$  and the third in  $E_2$ . The advantage of this interpretation is the better agreement of the spin-orbit splitting with the value 1.72 eV of the splitting of the ionization energies in the free  $Cs^+$  ion and a crystal-field splitting which is negligible when compared to spin orbit splitting. Besides this, it is not necessary to assume that excitonic structure associated with  $M_7^+(M_3)$  be hidden under the  $\Gamma$ -exciton bands.

A similar discussion as for CsI can be given for CsBr and CsCl. No band structure calculation, however, has yet been made. CsBr shows a structure very similar to CsI, whereas in CsCl  $C_1$  was not found and the identification of  $A_2$  and  $E_2$  is difficult. With decreasing atomic number of the halide a chemical shift for the prominent structure to higher energies is observed.

#### 4.1.3

The foregoing interpretation for the first two groups of excitations based on considerations concerning energy differences is not completely satisfactory in some respects. The calculated energy differences between the bands have to be strongly manipulated in some cases to fit to the experimental data. The assignments are not unequivocal. In the case of the Cs halides with simple cubic structure one can, for instance, even find arguments for  $A_1$  not being due to an excitonic transition to the s-like  $\Gamma_6^+(\Gamma_1)$  but to the d-like  $\Gamma_8^+(\Gamma_{12})$  and  $B_1$  to the s-like  $\Gamma_6^+(\Gamma_1)$ . This would be consistent with Onodera's band calculation in the unrevised form [8], where  $\Gamma_{12}$  lies below  $\Gamma_1$ . Moreover, the  $A_1$ - and  $A_2$ - ( $\Gamma_1$ )-lines do not show shifts to higher energies for lower temperatures. This is in contrast to other  $\Gamma_1$  excitons found in the  $Rb^+4p$ ,  $K^+3p$  and  $Na^+2p$  spectra or in valence band excitation. In these cases distinct shifts to higher energies are usually observed for the  $\Gamma_1$ -excitons when the temperature decreases [11, 19, 20]. Significant shifts to higher energies are only found for  $B_1$  and  $B_2$ .

For a thorough interpretation it is necessary to also consider the oscillator strength and the individual shape of the transitions. Moreover, the excitations above 16 eV have not yet been discussed. They are associated with higher conduction band states or metastable excitons. To understand these features in detail is a much more difficult task and demands further theoretical work.

#### 4.2 Ionic excitation

Another approach for describing the  $\text{Cs}^+ 5p$  spectra is by comparing them to the excitations of the free  $\text{Cs}^+$  ion (cf. Table 1 and 2). In the case of CsF (Table 1)  $A_1$  and  $A_2$  can be associated with the transitions  $\text{Cs}^+ 5p \rightarrow \text{Cs}^+ 6s$  [ $3/2$ ] and  $\text{Cs}^+ 6s'$  [ $1/2$ ] according to Moore's  $j_1$ -coupling notation [14]. - In comparison to earlier assignments using the ionic picture in interpreting room temperature reflection data [1] the assignment given here is somewhat modified. - With regard to the ionic transitions,  $A_1$  and  $A_2$  are both shifted to energies lower by about 0.5 eV. C,  $B_1$  and  $B_2$  can be attributed to the remaining three low lying dipole allowed transitions of  $\text{Cs}^+$ , namely  $\text{Cs}^+ 5p \rightarrow \text{Cs}^+ 5d$  [ $1/2$ ],  $\text{Cs}^+ 5d$  [ $3/2$ ] and  $\text{Cs}^+ 5d'$  [ $3/2$ ]. The absolute positions agree within 0.08 eV. The transition C, the first in the d-triplet, is of considerably smaller oscillator strength, as is also found for the  $np \rightarrow nd$  [ $1/2$ ] transition in rare gases [21] and likely in the  $\text{Rb}^+ 4p$  excitation spectrum [10, 11]. This seems to be a general feature for closed p-shell excitation.

For CsCl, CsBr and CsI the small peak at 12.6 eV preceding the most prominent exciton together with  $A_1$  and  $A_2$  may correspond to the ionic triplet  $5p \rightarrow 5d$  (Table 2). The ionic transitions, however, lie higher in energy by about 0.6 eV. As already mentioned in 4.1 it is difficult to find a spin-orbit mate for  $A_1$  in the case of CsCl.  $B_1$  agrees very well with the  $5p \rightarrow 6s$  [ $3/2$ ] transitions of the free ion. Only CsCl shows a larger difference (0.2 eV).

As compared to the ionic transition  $5p \rightarrow 6s'$  [1/2] the maximum  $B_2$  is shifted by 0.07 (CsCl), 0.53 (CsBr) and 0.54 (CsI) to lower energies. The assignments given for the fcc Cs-halides are in many respects consistent with those for CsF: all transitions assigned to  $5p \rightarrow 6s$  shift considerably to higher energies with decreasing temperature. All transitions  $5p \rightarrow 5d$  do not show significant shifts to higher energies at low temperature. The first transition associated with  $5p \rightarrow 5d$  has rather small oscillator strength.

Although the ionic picture seems to be quite useful in the interpretation of the Cs $5p$ -spectra it can only be considered as a rough first approximation. At present it does not explain all features of the spectra. For example, it cannot account for the structure between  $B_1$  and  $A_2$ , even if dipole forbidden transitions are additionally considered. Altogether, however, it seems today to be simpler and more effective than the considerations based on available band calculations. In the solid a crystal field potential due to the surrounding ions acts on the electrons of the  $Cs^+$  ion. It has lower, namely cubic symmetry as compared to the spherical symmetry of the free ion. This may cause observable splitting of levels which are degenerate in the free ion case. Crystal field effects should be studied quantitatively in order to improve the ionic picture and to explain how the energy levels and oscillator strength of the free  $Cs^+$  ion transitions are modified in the solid.

#### 4.3 Sidebands associated with the most prominent exciton

After having cooled the sample the most prominent peak in the  $Cs^+5p$ -spectra,  $B_1$  for CsF and  $A_1$  for the other Cs-halides, showed a distinct shoulder at the high energy side (Fig. 4). This interesting feature was also observed after annealing the evaporated films at  $150^\circ$  and for films evaporated on NaCl single crystals instead of a gold coated plate.

It may be related, to the sidebands recently observed for the first valence band excitons of several fcc alkali halides [22-24]. A possible explanation for the sideband is that it is caused by exciton-phonon interaction [25]. The distance of the shoulder from the main peak, however, is apparently larger than would correspond to an emission of a single optical phonon. The maximum phonon energies are 20, 14 and 11 meV for CsCl, CsBr and CsI respectively [26, 27]. Therefore, a recoil process or a more complicated exciton-phonon complex [25] has probably to be taken into account. On the other hand, single phonon emission may be observable under higher resolution and at even lower temperatures. For a thorough understanding of the sidebands one has additionally to consider several other possibilities which can produce similar fine structure. In the case of valence band excitation they have recently been discussed in detail [22, 24].



## 5. Summary

The reflection spectra of evaporated films of all Cs halides were measured at 30 K for photon energies between 12.5 and 26 eV in order to investigate the excitation of the  $\text{Cs}^+5p$  level. The spectra show a great number of maxima, especially at low temperature. The low lying sharp maxima were interpreted as excitons coupled to critical points in the Brillouin zone and in a complementary approach by comparing the excitations with transitions of the free  $\text{Cs}^+$  ion, i.e. in terms of localized excitons. Neither approach is completely satisfactory. Neither approach can explain all spectral details. The second approach, however, seems to account more directly for the observed excitations. As far as the first approach is concerned calculations of the conduction- and  $\text{Cs}^+5p$  band together with density of states are necessary to separate, if possible at all, single particle and excitonic effects. On the other hand, it would be desirable to learn from model calculations whether the free  $\text{Cs}^+$  ion transitions can be influenced by the potential of the surrounding ions in such a way that the experimental spectrum be explained.

The measurements reported here should be repeated at even lower temperatures and with even higher resolution. It might then be possible to fully understand the electronic transitions from the  $\text{Cs}^+5p$  level, especially those which seem to be strongly coupled to lattice vibrations as is indicated in the observed asymmetric profile of the most prominent  $\text{Cs}^+5p$  exciton.

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Figure Captions

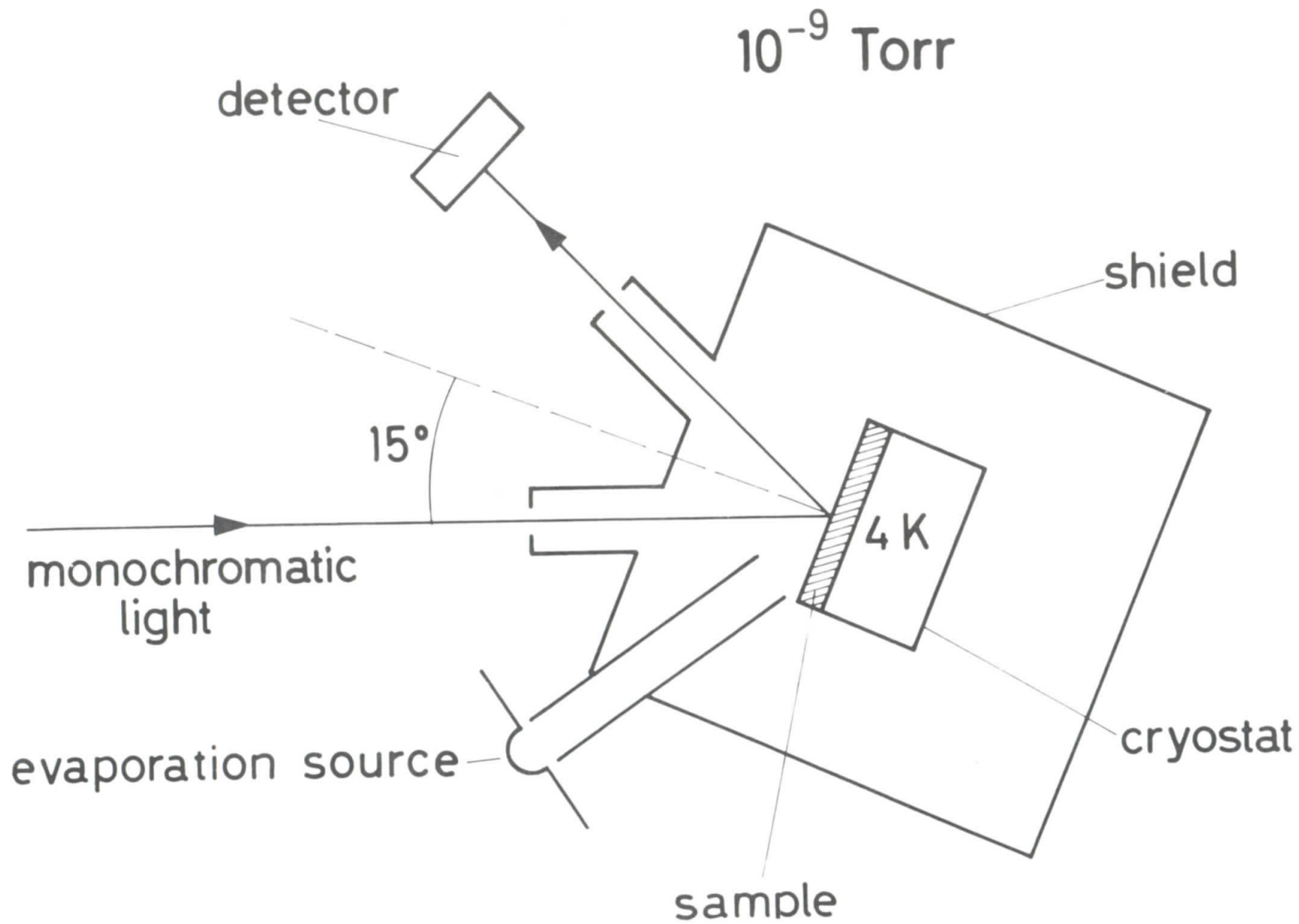
- Fig. 1 Sketch of the experimental set-up for the reflection measurements at low temperatures under ultrahigh vacuum.
- Fig. 2 Reflection spectra of all Cs halides at room temperature and at 29 K. For every halide the spectra for the two temperatures are adjusted to 1.0 at the highest peak. The reflectivity at 29 K is actually higher than at room temperature (see text).
- Fig. 3 Reflection spectra above 165 eV. The arbitrary units for the reflectance follow the convention of Fig. 2.
- Fig. 4 The most prominent exciton line with sideband in an extended energy scale at 29 K. The position of the peaks and the separation of the sideband is given in eV.
- Fig. 5 Comparison of reflection and recent absorption spectra for CsCl. S+S this work, S ref. 3, B+R ref. 4.
- Fig. 6 Comparison of reflection and recent absorption spectra for CsI. S+S this work, S ref. 3, B+R ref. 4.
- Fig. 7 Band structure of CsF according to reference 7. The Cs5p band has not been calculated. It is schematically drawn analogous to the valence band. VB = valence band, CB = conduction band.
- Fig. 8 Band structure of CsI according to reference 8, revised form. The Cs5p band has not been calculated. It is schematically drawn analogous to the valence band. VB = valence band, CB = conduction band.

Table 1: Position of maxima and shoulders (s) in eV found in the reflection spectra of CsF at 29 K and at room temperature (in brackets). The ionic excitation energies are taken from reference 14. The last column gives tentative assignments of the transitions to critical points.

CsF			ionic excitations Cs <sup>+</sup> 5p <sup>6</sup> →		critical points
13.03	(12.89)	A <sub>1</sub>	6s [3/2]	13.37	Γ <sub>8</sub> <sup>-</sup> (Cs5p)→Γ <sub>1</sub>
13.25	(13.23)	C	5d [1/2]	13.17	
13.71	(13.74)	B <sub>1</sub>	5d [3/2]	13.75	
14.54s					
14.69	(14.59)	A <sub>2</sub>	6s' [1/2]	15.23	Γ <sub>6</sub> <sup>-</sup> (Cs5p)→Γ <sub>1</sub>
14.87s					
15.30	(15.37)	B <sub>2</sub>	5d' [3/2]	15.32	
15.96					
16.56s					
17.28s					
17.74	(17.76)				
18.64	(18.84)				
20.35					
21.03					
22.24s					
25.91	(26.07)				

Table 2: Position of maxima and shoulders (s) in eV found in the reflection spectra of CsCl, CsBr and CsI at 29 K and at room temperature (in brackets). The ionic excitation energies are taken from reference 14. The last column gives tentative assignments of the transitions to critical points.

CsCl		CsBr		CsI		ionic excitations Cs <sup>+</sup> 5p →		critical points	
12.62	(12.64)	12.67	(12.62)	12.51s		5d [1/2]	13.17		
13.22	(13.23)	13.12	(13.11)	13.06	(13.15)	A <sub>1</sub>	5d [3/2]	13.75	Γ <sub>6</sub> <sup>-</sup> (Cs5p) → Γ <sub>1</sub>
13.58		13.36		13.35	(13.26)s	B <sub>1</sub>	6s [3/2]	13.37	Γ <sub>6</sub> <sup>-</sup> → Γ <sub>12</sub>
		13.80s		(13.74)s	13.68		C <sub>1</sub>		
14.11	(14.10)s	14.07	(13.97)	13.93	(13.92)	D <sub>1</sub>			M <sub>6</sub> <sup>-</sup> (Cs5p) → M <sub>1</sub> M <sub>7</sub>
14.37s	(14.35)								
14.63	(14.63)	14.49	(14.44)	14.43	(14.43)	E <sub>1</sub>			M <sub>6</sub> <sup>-</sup> (Cs5p) → M <sub>5</sub> M <sub>7</sub>
14.94s	(15.06)s	14.70	(14.77)	14.69	(14.85)	A <sub>2</sub>	5d' [3/2]	15.32	Γ <sub>6</sub> <sup>-</sup> (Cs5p) → Γ <sub>1</sub>
15.16		14.92		14.96		B <sub>2</sub>	6s' [1/2]	15.23	Γ <sub>6</sub> <sup>-</sup> (Cs5p) → Γ <sub>12</sub>
15.37s									
15.71s		15.35s		~15.09s		C <sub>2</sub> D <sub>2</sub>			M <sub>6</sub> <sup>-</sup> (Cs5p) → M <sub>3</sub> , M <sub>1</sub>
15.85									
16.16									
16.40s		16.08s		15.98s	(15.96)s	E <sub>2</sub>			M <sub>6</sub> <sup>-</sup> (Cs5p) → M <sub>5</sub>
16.77	(16.75)	16.45	(16.34)	16.21	(16.33)				
				16.40					
17.26	(17.71)	17.09	(17.28)	16.89	(16.98)s				
17.69		17.48							
18.70	(18.70)	18.56	(18.42)	17.83	(17.80)s				
~19.49s		18.96s		18.44s					
20.32s	(20.23)s	20.13		19.38	(19.40)s				
		20.55							
		21.28							
23.09	(23.17)	21.81	(21.34)s	20.52s	(20.44)s				
		22.51s							



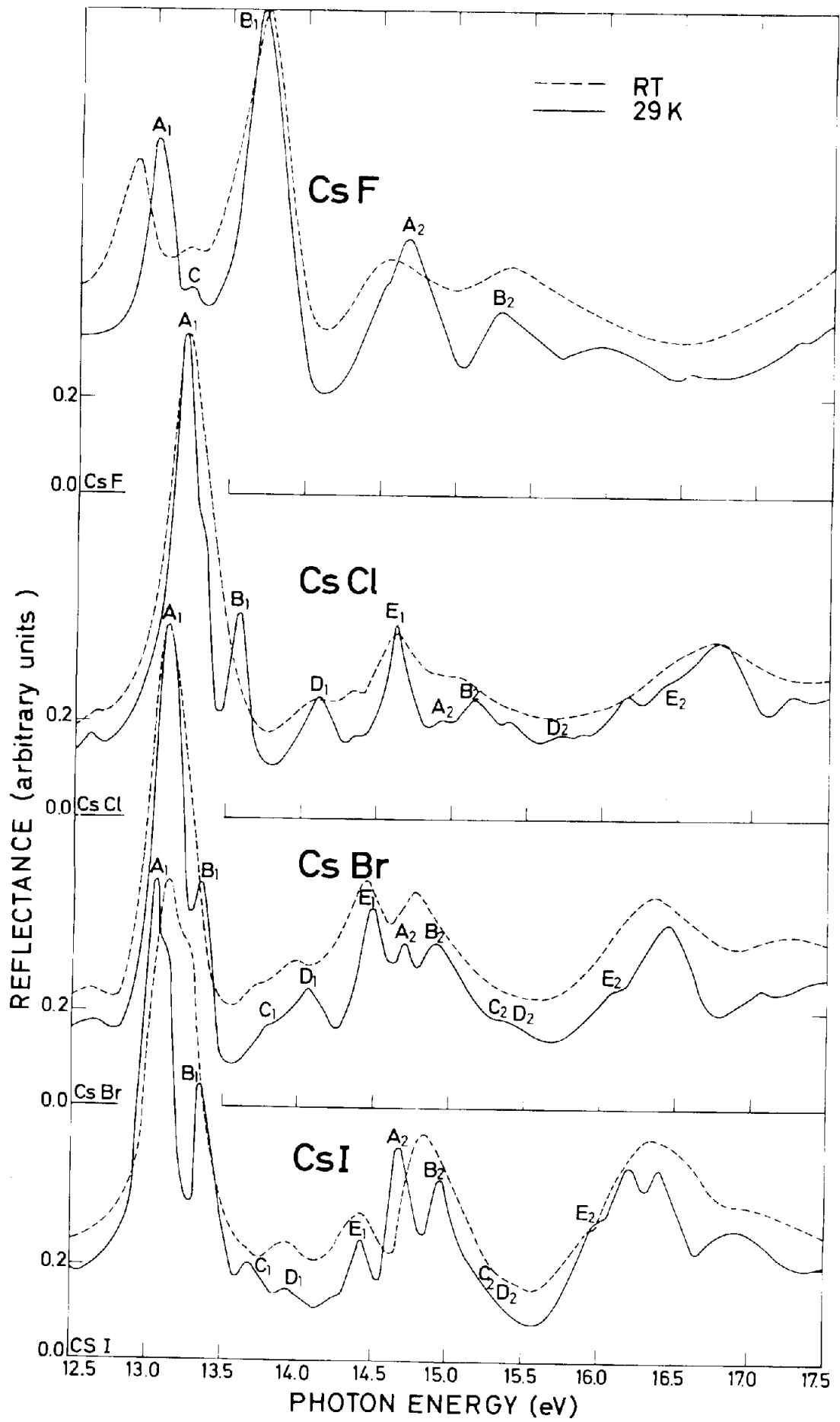


Fig. 2



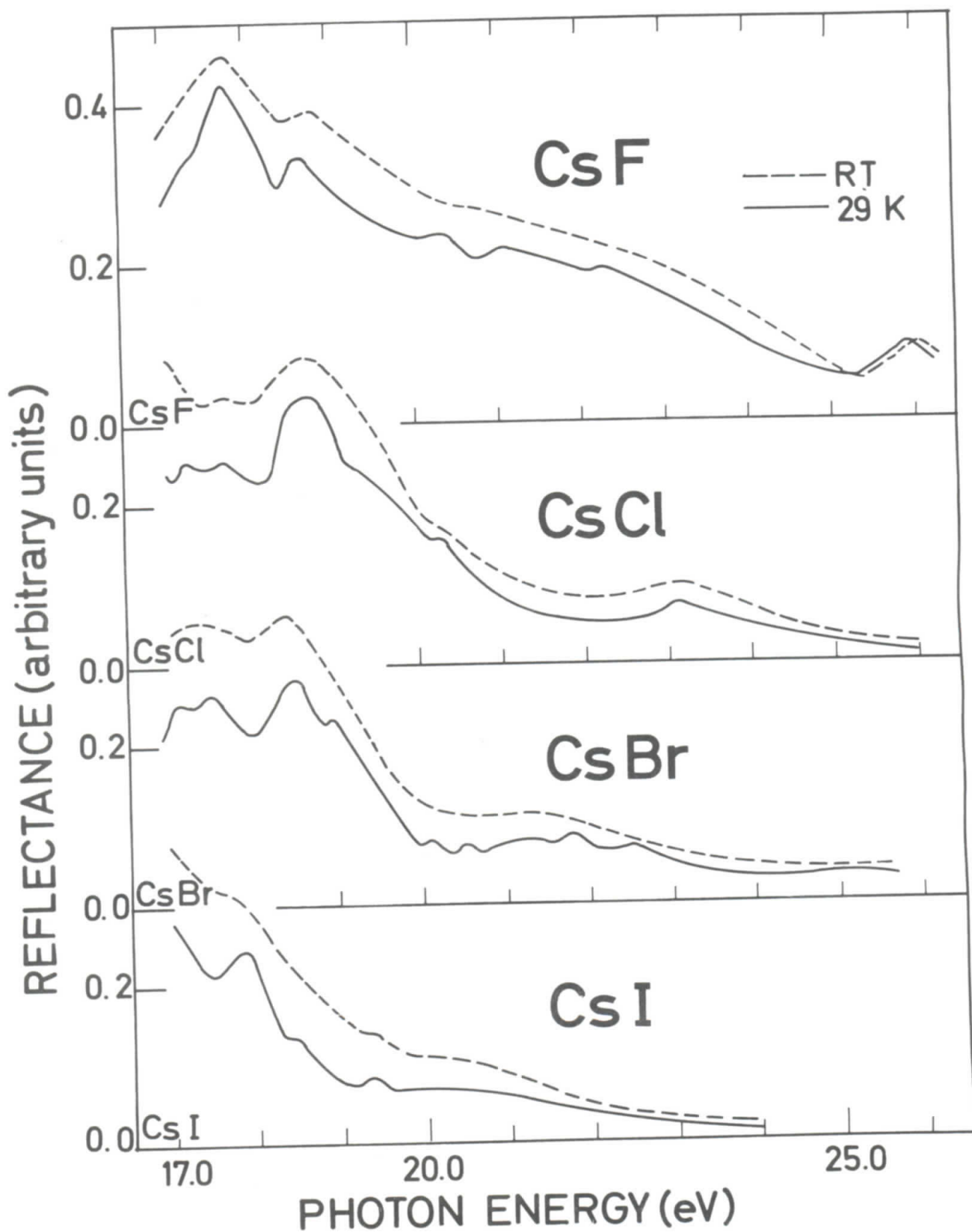


Fig. 3

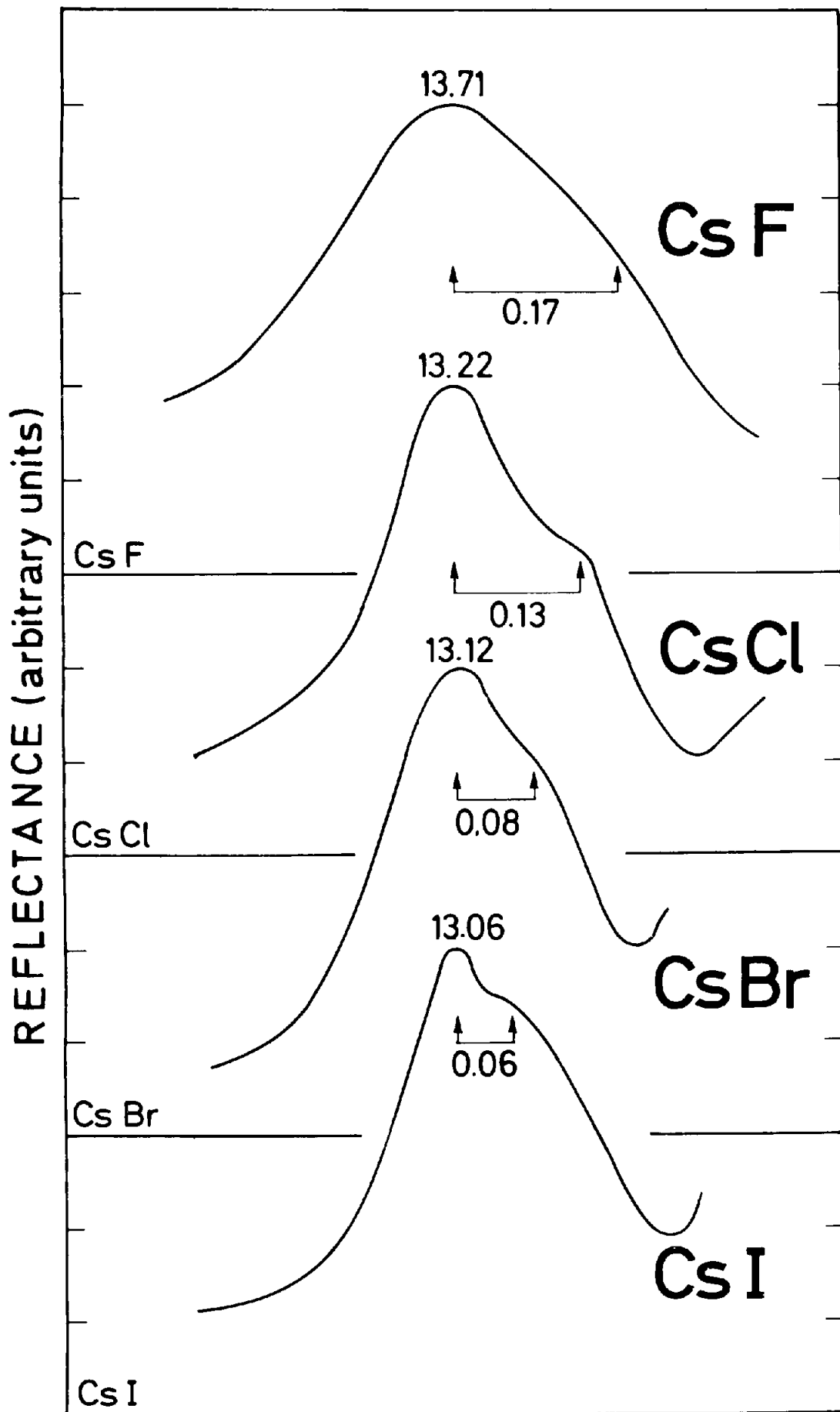


Fig. 4

Fig. 5

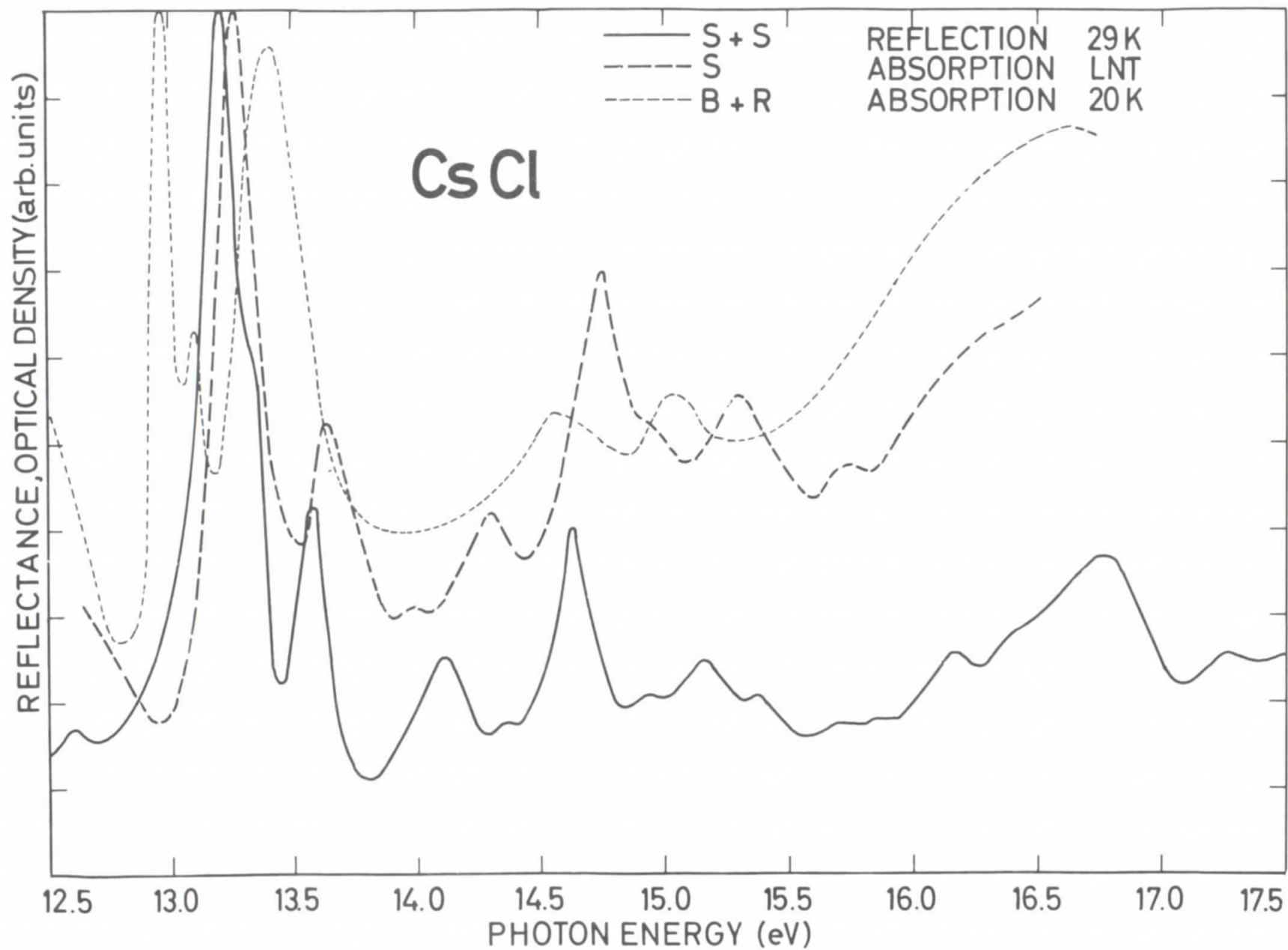
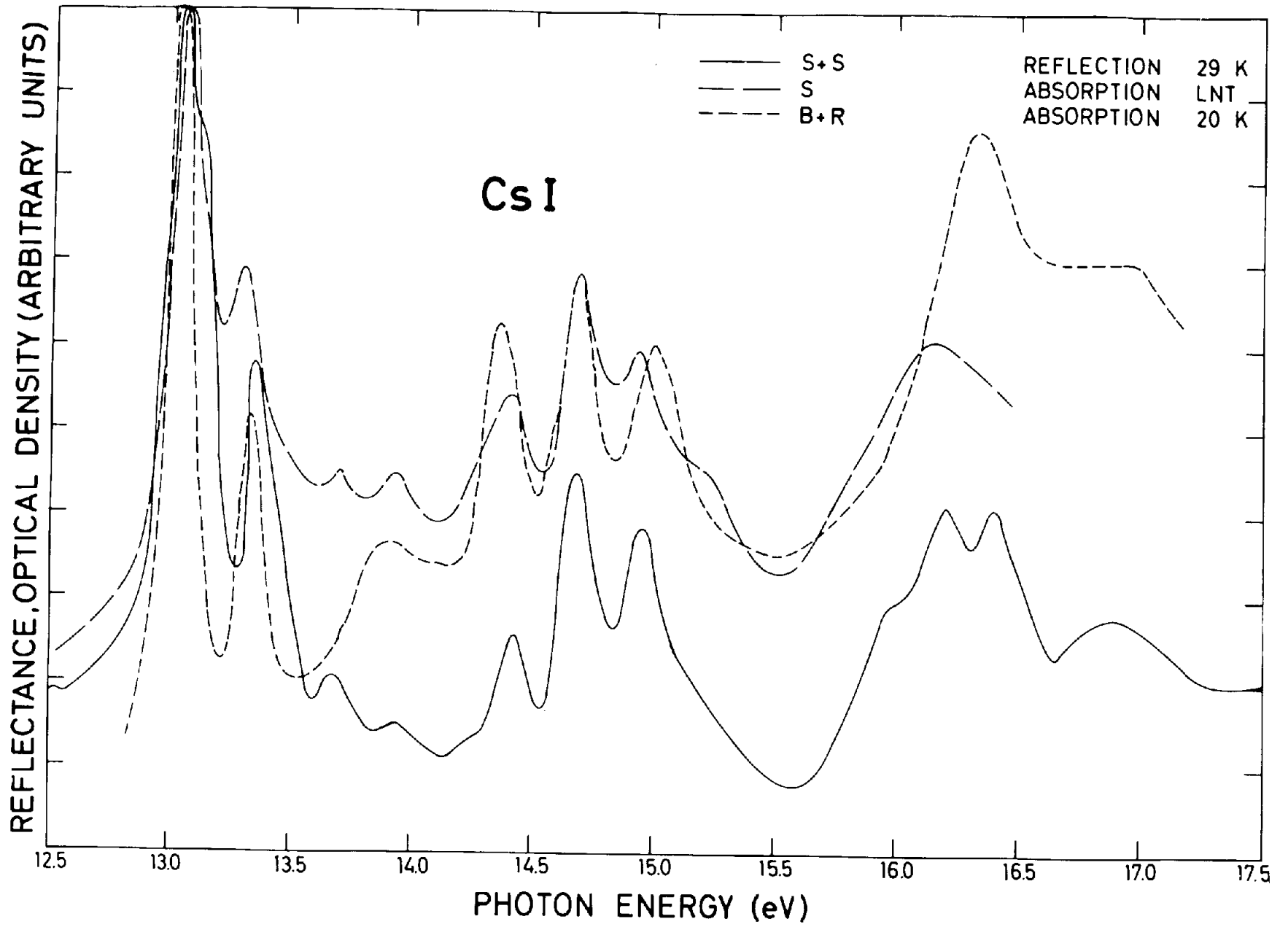


Fig. 6



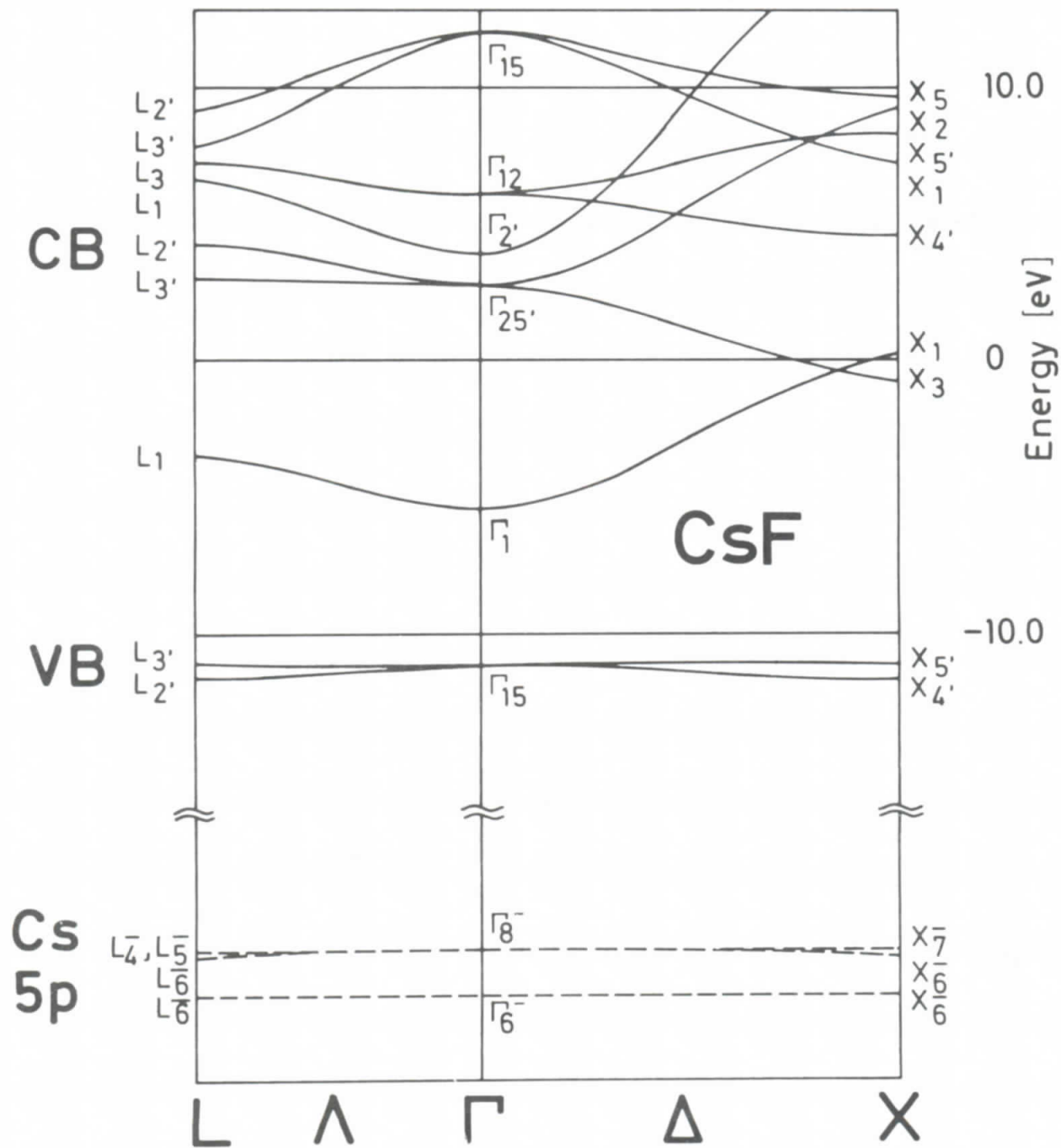


Fig. 7

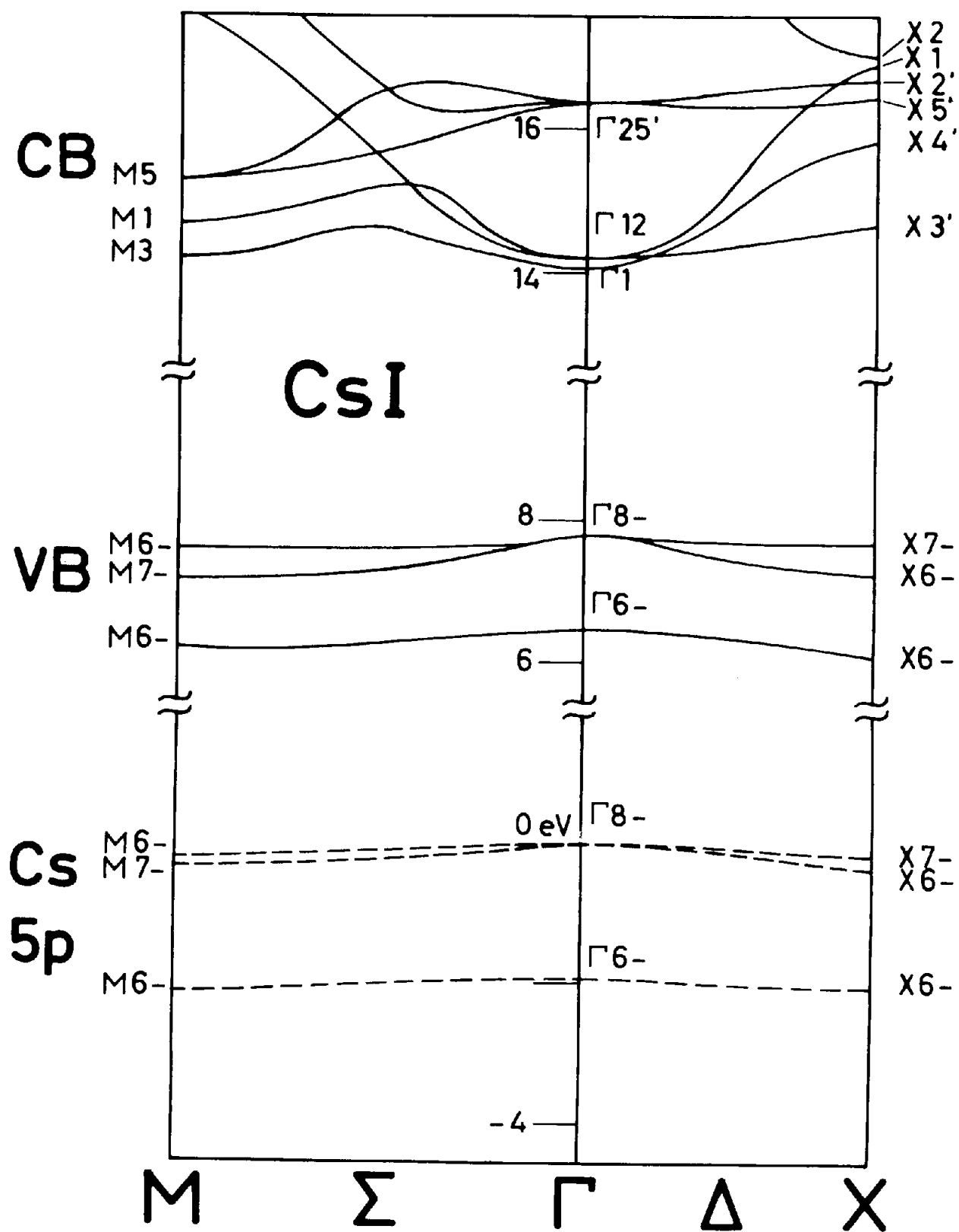


Fig. 8