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Electron Hole Interaction in Deep Level Spectra

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Electron Hole Interaction in Deep Level Spectra

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Optical absorption, reflection and photoelectric yield spectra of solids in the vacuum ultraviolet are shaped by both one-electron interband transitions and excitations to bound electron-hole states. In addition, the electron-hole interaction can also modify or even determine the shape of the spectra above the ionization limit. The identification of electron-hole effects is of fundamental importance for the interpretation of the spectra and also for the correct extraction of bandstructure information. Recent progress in this respect for insulators, semiconductors and metals is described. The role of the electron hole interaction for surface excitations is also briefly discussed.

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1. Introduction

The intensive experimental investigation of absorption coefficients of solids in the vacuum ultraviolet[1-8] which is now in progress for about ten years was accompanied all the time by the problem of separating those effects which are due to the electron-hole interaction from those which are mainly determined by one-electron interband transitions[9]. The interband transitions are of a more practical importance since they can lead to a determination of the optical density of states, which lends itself to a more or less direct comparison with - and improvement of - band structure calculations. The electron-hole interaction, on the other side, is of fundamental theoretical interest since it provides information on two-body and many-body correlation effects. Although considerable insight into these problems has been gained many questions are still open. New experimental techniques of investigating these problems have recently been demonstrated. In this survey paper several recent results on insulators, semiconductors, and metals will be discussed. While volume properties usually are investigated by absorption spectroscopy, reflection spectroscopy, and photoelectron yield spectroscopy, the latter technique is also very sensitive to surface excitations, especially when selecting fast electrons which have a short mean free path for electron-electron scattering.

Electron-hole interaction in deep level spectra can manifest themselves in several different ways.[5,7] There are (i) the intraatomic correlation effects such as multiplett-splitting in the case of solids made up of atoms with incomplete d and f shells or there are giant resonances. These effects are treated in the accompanying papers on atomic physics. Another kind

(ii) are the genuine two body effects like excitons which we shall be concerned with in this paper. In this case the electron-hole interaction can be accompanied by so-called inner-well resonances. Finally (iii) genuine solid-state many-body effects occur, like the edge anomalies in the spectra of light metals and we shall treat also these effects here.

This paper cannot give an exhaustive review. The present experimental situation will be demonstrated on a few examples in each of the categories: insulators (Section 2), semiconductors (Section 3), metals (Section 3), and surfaces (Section 4).

2. Insulators

The simplest idea in describing the effects of the electron-hole interaction in insulators and semiconductors is that of an exciton, namely a bound electron-hole state. The ordinary exciton bound at the fundamental band gap is a very mobile entity due to almost equal effective masses of the electron m_e and the hole m_h, which are in the order of magnitude of the free electron mass m. Excitons for which the electron is bound to a fairly imobile core hole are, however, describable by essentially the same models.

The simplest model which takes into account the electron hole interaction in a solid is the Wannier-Mott exciton[10]. In this model the electron is bound to the hole in hydrogen-like states according to

$$E_n = E_I - \frac{\mu}{m} \frac{1}{\varepsilon^2} R \frac{1}{n^2} \qquad (1)$$

where E_I is the ionization energy of the hole level (e.g. the energy needed to excite the electron to the lowest conduction band state), μ/m the ratio of the reduced electron-hole mass versus the free electron mass, R=13.6 eV (the Rydberg constant) and ε^2 a low frequency dielectric constant.

The excitation of such bound exciton states is schematically shown in Fig. 1. While excitons in narrow band gap semiconductors usually have a very large radius, due to a large screening of the Coulomb interaction by a large dielectric constant - the first series member (n=1) in insulators is spatially very small. This leads to several corrections to the excitation energy as given by Eq. (1), which are called central cell corrections: a) smaller dielectric constant, b) different effective mass, c) exchange repulsion from the core region. Fig. 2 shows a well developed exciton series in the absorption spectrum of solid Ne[11,12]. The parameters obtained from a fit of (1) to the $n \geq 2$ lines are: E_I=21.69 eV, $\mu/m \cdot 1/\varepsilon^2 \cdot R$=5.24 eV. The binding energy of the n=1 line is by 1.04 eV smaller than calculated with these parameters, which gives an idea of the net central cell corrections. It should be mentioned that the effects a)-c) act in different directions and partly cancel each other. With ε=1.25[12] one can compare the effective electron and hole masses with those obtained from typical band structure calculations. Kunz and Mickish[13] give $m_h \approx 10$, $m_e \approx 0.8$. With m_h=10 the experimental result is m_e=0.64 which can be considered to be a good agreement with theory.

Instead of the effective mass approach of the Wannier-Mott exciton, which necessitates knowledg of the band structure as mentioned above, and the additional central cell corrections needed for a satisfactory description of the first member of the series, one can set out with atomic or molecular resonance excitations. The rest of the crystal is then treated as a perturbation[14]. This leads to the Frenkel-Peierls exciton. The close correspondence frequently encountered between the VUV spectra of solids and those of the constituent atoms, or ions, or molecules makes this approach very promising.

In Fig. 3 we demonstrate how closely the first optically allowed excitations from the Li 1s level to the 2p states of the free Li^+ ion[15] coincide with the strong prominent peak at 62 eV in the LiF absorption and photoelectric yield spectra.[16,17]. This looks like a good example of a Frenkel-Peierls exciton.

LiF belongs to the simplest ionic crystals since its constituents are light atoms with only a few electronic states filled. Therefore it appears to be a good candidate for testing theoretical calculations. The astonishing result is that ϵ_2 from a Hartree-Fock-Slater self-consistent-field (SCF) band structure calculation by Menzel et al[18] closely reproduces the main structure which we associated in the last section with an exciton (see Fig. 3). The same holds for an ab initio Hartree-Fock SCF bandstructure calculation by Kunz et al.[19]. Their result originally places the onset of the Li^+ 1s transition at about 73 eV. Corrections due to polarization effects and electron hole attraction were applied as a rigid shift of about 20 eV, which again leads to a fairly good agreement with the experimental structures (see Fig. 3). This correction procedure has been subject to criticism[17]. Fig. 3 demonstrates the paradoxical situation that the two different concepts of bound states and band structure appear to apply to the same spectral features.

One intriguing feature in both the experimental and the theoretical spectra are the weak features which appear to set in at about 55 eV (Fig. 3). These would correspond to transitions to the s-symmetric states at the bottom of the conduction band in a band picture. These transitions are only weakly allowed due to atomic selection rules. In an exciton picture they correspond to bound states originating from transitions to Li^+ 2s states. Fields et al.[20] recently have investigated LiF by electron energy loss measurements. At large momentum transfer the optical dipole selection rules should break down, which manifests itself in changes of peak intensities. They come to the conclusion that the transitions to final states of s symmetry set in

at around 60 eV. In this case the weak features between 55 and 60 eV might either belong to valence band transitions or they are surface excitons (see below).

One important question in connection with spectra like those of LiF, where no Wannier series is identifiable, is with respect to the position of the bottom of the conduction band. Cudat et al.[17] and Pantelides and Brown[21] obtain the core level to valence band separation from UPS or XPS photoelectron spectra. Adding to this figure the band gap energy they obtain 63.8 eV for the onset of the Li 1s to conduction band transitions[17]. This value is indicated in Fig. 3. It allows to evaluate binding energies for the features near the onset of optical transitions between 2 and 8 eV. It is evident from this result that the prominent maximum at about 62 eV is a bound state, a Frenkel-Peierls exciton and cannot be a band-structure feature as it was assumed on the basis of band-structure calculations[18,19].

Now, after it has become clear which of the structures in Fig. 3 fall below the bottom of the conduction band E_c the next question is concerned with the nature of the structures above E_c. Are these peaks density of states-maxima, are they quasi-bound electron-hole states corresponding to higher critical points in the conduction band (metastable excitons[22]), or are they collective excitations (excited electronic polarons[23]). A recent investigation of the analogously structured Na^+ 2p excitation spectrum of NaCl provides some insight into this problem[24].

Figure 4 shows partial yield spectra of NaCl in the region of the Na^+ 2p transitions[24]. For measuring these spectra the energy of an electron-analyzer E_f was fixed and the photon energy scanned (constant final state spectra: CFS). While scanning at $E_f = 0$ the features in the spectrum closely resemble those of an absorption spectrum[25,26] or of a total yield spectrum[27] due to core hole decay and secondary scattering processes[28]. The spectrum is augmented by the peak of unscattered electrons excited directly into the energy window (at $E_f = 0$ in this case) of the electron analyzer. This peak is marked by a vertical dash in this spectrum and likewise its extrapolated position is marked in all the following spectra.

A similar analysis to the one for LiF gives the location of the bottom of the conduction band as 35.9 ±0.3 eV [24] in close agreement with Ref. 21. Peaks A, B and the triplet C thus are bound excitons. Since the electron affinity is about zero the directly excited peak at $E_f = 0$ is practically coinciding with E_c. What about the fairly sharp peaks D - H? It is recognized from Fig. 4 that a well developed peak of directly excited electrons appears for $E_f \gtrsim 6$ eV. This peak is equivalent to a Na^+ 2p line in an EDC, its large width being now understood[29,30] as a special kind of phononbroadening. In the spectra for $E_f < 6$ eV this peak is not readily discernible and the spectra are distorted. The most interesting feature in those spectra is a much stronger appearance of the peaks D - G not only when the final state channel hits a peak ($E_f = 0$ and 1.2 eV (D), $E_f = 3.5$ eV (E), $E_f = 4.5$ eV (F)) but also when E_f is close to but lower in energy than the peak. This is e.g. to be seen at $E_f = 4.5$ eV where F' is at a 1.5 eV higher energy, or in the $E_f = 1.2$ eV spectrum with peak E which lies at a 1 eV higher energy there. In the other spectra the same effect is also evident.

We now want to analyze this result according to a suggestion by Åberg and Dehmer[31]. The electrostatic potential of the Na^{++} ion, which has a potential wall built around it due to the exchange repulsion of the electrons sitting at the neighboring Cl^- ions, gives rise to a potential well which is capable of holding bound and quasi-bound inner well resonance states. This is depicted schematically in Fig. 5. There is only a low probability for a decay into an extended band state. During its relatively long lifetime the inner-well state relaxes with the accompanying emission of many phonons. This would explain the shift down in kinetic energy as observed in the spectra of Fig. 4. Peaks D - G therefore correspond to quasi-bound electron hole states above the bottom of the conduction band.

3. Semiconductors

In semiconductors the strength of the long range Coulomb interaction is considerably reduced - in the order of 1/100 - due to dielectric screening according to Eq. (1). General theories for e.g. Si estimate the binding energy for the Si 2p excitonic final state to be of the order of 40 meV[32,33]. There is, however, the fundamental question with respect to the magnitude of the central cell corrections for the n = 1 exciton. If for the n = 1 exciton the electron is localized completely within the cell defined by the nearest neighbors, these corrections could be as large as ~ 1 eV. The major correction we have in mind is the one due to the absence of screening inside this cell. The situation is schematically visualized in Fig. 6. The binding energy of the n = 1 state depends very critically on the position of the transition point (marked TP) where the unscreened potential meets the screened potential.

Many attempts have been made to investigate the electron hole interaction at the threshold for 2p transitions at ~ 99.9 eV. Fig. 7 shows the onset of these transitions as determined by Brown and Rustgi[34] on crystalline Si. The contributions of the two spin orbit components L_2 and L_3 were obtained by deonvolution. For comparison the density of states as calculated by Kane[35] is given. There is a reasonable agreement between the calculated and measured positions fo the maxima. But it is also evident that the threshold behavior is in disagreement. The experimental absorption coefficient rises sharply, whereas the slow increase of the density of states extends over almost 2 eV. The inclusion of k-dependent matrix elements does not resolve this discrepancy[36]. No separate exciton peaks are observed in the experimental spectrum. This, however, cannot be expected at room temperature if the binding energy is in the order of 40 meV.

Altarelli and Dexter[32] have applied the effective-mass theory[10], which describes not only the bound states according to Eq. (1) but also the effects of the electron-hole attraction on the continuum transitions. They obtained good agreement with the experiment up to an energy 0.6 eV above threshold. Only the absolute value of the absoprtion coefficient is too small from the effective mass approximation by a factor of ~ 10. Since the absorption coefficient is proportional to the square of the "envelope function" $F(0)^2$ at the origin[10], which is a measure of the probability of finding the electron near the hole, this - according to Fig. 6 - could be an indication of a much stronger local potential than assumed by Altarelli and Dexter[32]. As a further consequence the 40 meV binding energy for the n = 1 exciton could be drawn into doubt. Several investigations were concerned with this problem:

It was attempted by several authors to obtain exciton binding energies by combining XPS photoemission and absorption coefficient (resp. energy

loss data[34,37,38] in the same way as it was demonstrated for insulators in sections 2. The required measuring accuracy for semiconductors is, however, much larger since the exciton binding energies are small. This explains why there is much divergence in the results of different authors: 0.6 ±0.2 eV[37], 0.9 ±0.4 eV[38] for the exciton binding energy.

Brown et al.[39] tried to observe the change in binding energy with highly doped Si (~ 10^{20} donors per cm^3) which was practically metallic. Such a doping produces a screening length of ~ 20 Å. No shift of the apparent Si 2p edge was observed proving that the states involved at the onset of the 2p transitions are more local than 20 Å. This result was recently confirmed by Eberhardt et al.[40] with samples of even higher doping.

Finally, an attempt has been made to observe the electroreflectance spectrum at the Si 2p edge[37,41]. No detectable signal in $\Delta R/R$ with a sensitivity of 10^{-4} for a $3 \cdot 10^5$ V/cm modulation was observed. Applying effective mass theory[42] the authors conclude that the exciton binding energy must be at least 300 meV.

Whereas all these results indicate a fairly large exciton binding energy in the order of 0.5 eV it is not conceivable why then an exciton peak at the edge cannot be observed in the absorption spectra.

The exciton problem is also of fundamental importance for the interpretation of the spectra of other semiconductors, namely those of the Ga-V compounds[41,43,44] and of lead compounds[45] among others. While Aspnes <u>et al.</u>[41,43,44] assume exciton binding energies in the order of 100 - 200 meV for the Ga 3d excitations in their electroreflectance measurements and then proceed with an interpretation in terms of critical points in the band structure picture Martinez et al.[45] find binding energies of 0.9 eV for the Pb 5d excitations. They doubt that their second derivative reflectivity spectra (which show many sharp structures) can be interpreted in terms of critical points at all.

4. Metals

The most efficient screening of the Coulomb potential of the core hole is accomplished in a metal (see Fig. 6). While only the long-range part is screened (we ignore here Friedel oscillations), there remains a truncated Coulomb potential inside a sphere with a radius in the order of 1 Å. This potential is not capable of binding an electron in a resonance state, but the excited electron and all the metal electrons undergo scattering processes and infinitesimal energy changes because of the sudden creation of this potential (see Fig. 8). The scattering of the electrons can be described in terms of phase shifts in a partial wave analysis. Depending on the values of these phase shifts and the symmetry character of the core hole (s, p, d...) the shape of the absorption edge is in the asymptotic region right at the edge predicted according to a theory due to Mahan[46] and Noziéres and De Dominicis[47]. The same model also descirbes the asymmetry in line shape of photoemission lines of core levels[48].

We do not want to elaborate on the details of this theory here but refer to a series of reviews dealing with this topic on different levels[49,5,7]. Especially the applicability of the model to the observed spectra (mainly of alkali and light metals)has been questioned (see e.g. Ref. 50). Even if applicable there is no agreement on the energy range away from the edge in which the edge shape laws[49] should apply. These laws predict a spike right at p edges in cases like e. g. the 2p edge of Na metal and a rounding at s edges like e. g. at the 1s edge of Li metal.

Fig. 9 shows the Na 2p absorption spectrum[51]. A striking feature is the prominent sharp spike right at the edge which cannot be mistaken as a density of states features since, as it is well known, the density of states is free electron like at the Fermi energy in Na. Further, this peak, unlike the peaks C and D persists in the spectrum of liquid Na. In a simplified description the spike can be considered as an exciton with zero binding energy superimposed on the absorption edge. The 3p edge of K, the 4p edge of Rb and the 5p edge of Cs have recently been measured by Ishii et al.[52]. All these edges exhibit the spike phenomenon, the sharpness decreasing from Na to Cs.

The rounding of 1s edges like that of Li competes with other rounding processes like Auger and temperature effects. Therefore this manifestation of the electron hole interaction is by far more difficult to proove. In the case of Li a large rounding seems to have been simulated by a density of states effect[53] while the actual rounding is obviously much smaller.

5. Surfaces

Core electron excitations at surface atoms are applied more and more to investigate surface properties. Eastman and Freeouf were the first to use surface sensitive partial yield spectroscopy for the investigation of surface states on Ge[54], Ga Sb[55] and other semiconductors[55]. They found surface contributions preceeding the onset of volume transitions, which therefore appeared to correspond to transitions into an empty surface band, which would be located in the volume band gap. Fig. 10 shows the surface peaks in the Ga 3d spectrum of GaSb. It is noteworthy that these states are not present when exciting from the Sb 4d level. This implies a strong localization of these surface excitations at the Ga atoms and could be interpreted in terms of surface states built from unoccupied Ga dangling bonds.

Lapeyre and Anderson[56] were able to demonstrate by measuring the direct recombination process of the electron with its hole in GaAs that these excitations are not one electron transitions into an empty surface band but surface excitons. Their ionization line probably corresponds to a surface band, the binding energy, however, has not yet been determined. This interpretation was lateron confirmed by a detailed investigation of the position of the surface Fermi energy by Gudat et al.[57,58]. For further details see Ref. 59. In this context it is interesting to note that electron energy loss measurements at the Si 2p threshold reveal two surface peaks[38] which show an excitonic shift of 1 – 2 eV.

Surface excitons have also been shown to exist on the surfaces of insulators. Saile et al.[60] have found surface excitons for several rare gas solids, when measuring the absorption of relatively thin films ($\sim$50 Å).

In addition to the volume excitons surface sensitive peaks are excited on e. g. Ar at a $\sim$0.5 eV lower photon energy. These peaks disappear with a thin Kr overlayer. The picture of a surface exciton appears to be quite adequate for these new features. The binding energy is increased. This would be expected for an electron bound to a hole on a surface atom since the dielectric screening is reduced. A more detailed theoretical treatment based on the model of a surface molecule is needed for interpreting the splitting of the surface exciton line[61].

Bound states at the surface of ionic crystals were shown to exist on Mg O by means of energy loss excitation from the Mg 2p level[62] and further with retarding field partial yield spectroscopy on (100)cleavage surfaces of NaCl[63]. Fig. 11 shows these spectra which are different when exciting with s and p polarized light. This demonstrates that localized bound states with different symmetries relative to the NaCl (100) surface are involved. These states have up to 0.6 eV larger binding energies than the excitons at the onset of the Na^+ 2p transitions. Again calculations considering the local geometry around a Na^+ surface ion are needed for a detailed interpretation of the spectra[61].

6. Conclusion

Quite obviously the electron hole interaction is a strong perturbation of the volume and surface one-electron band picture. In many cases the band aspects are not only perturbed but completely destroyed and a local picture appears to be more adequate. The emerging phenomena deserve an interest in their own right since they provide considerable insight into two-body and many-body effects.

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Figure Captions

Fig. 1 Optical transitions in metals and insulators, schematic. The density of states N(E) is indicated towards the right. E_F = Fermi energy, CB = conduction band, VB = valence band, Ex, exciton (from Ref. 7).

Fig. 2 Absorption coefficient of solid Ne showing a Wannier exciton series converging to the band gap energy E_G (from Ref. 12).

Fig. 3 Experimental photoelectric-yield (heavy solid line) spectrum[17] and experimental absorption coefficient[16] (thin solid line) compared with the calculated ε_2 spectra of Menzel et al.[18] (dashed line) and Kunz et al.[19] (dash-dotted line). The vertical bars give the energy positions of transitions in the Li^+ ion according to Moore[15]. E_c marks the bottom of the conduction band (after Ref. 17).

Fig. 4 Constant final state spectra from a d = 70 Å thick NaCl film. E_f is the final state energy relative to the bottom of the conduction band. E_c marks the bottom of the conduction band. The heavy vertical bars give the positions of the channel of directly excited electrons in each spectrum (from Ref. 24).

Fig. 5 Schematic diagram illustrating inner well states in the effective potential around the Na^{++}-ion due to the repulsion of electrons from the Cl^- ions. The letters A - G correspond to the peaks in the spectra of Fig. 4 and the position of these levels anticipates the analysis of the spectra of Fig. 4 (from Ref. 24).

Fig. 6 Schematic radial dependence of an unscreened (upper), dielectrically screened (middle), and metallically screened (lower) potential V(r). The free potential is capable of binding electrons in Rydberg states (1, 2, 3, 4...) converging to E_c (free), the screened potential has bound states (1', 2', 3'...) converging to E_c (s.c.). In the latter case the binding energy of the n = 1' state depends crucially on the position of the transition point TP from the screened to the unscreened potential which is near the surface of the Wiegner-Seitz cell. The hole potential inside a metal usually cannot bind an electron, it gives rise however to electron scattering.

Fig. 7 $L_{2,3}$ absorption spectrum of crystalline Si. The L_2 and L_3 components and the density of states of the conduction band[35] (dashed line) are included (from Ref. 34).

Fig. 8 Shielding of a suddenly created core hole in a metal
(a) in space and
(b) in an energy picture
(from Ref. 5).

Fig. 9 Photoabsorption and photoelectric yield of solid and liquid Na metal in the region of 2p transitions (from Ref. 51).

Fig. 10 Partial yield spectra for a (110) Ga Sb surface for Ga 3d transitions and for Sb (4d) transitions. E_v = top of valence band, E_c = bottom of the conduction band, Δ = spin orbit splitting of Ga 3d (from Ref. 55).

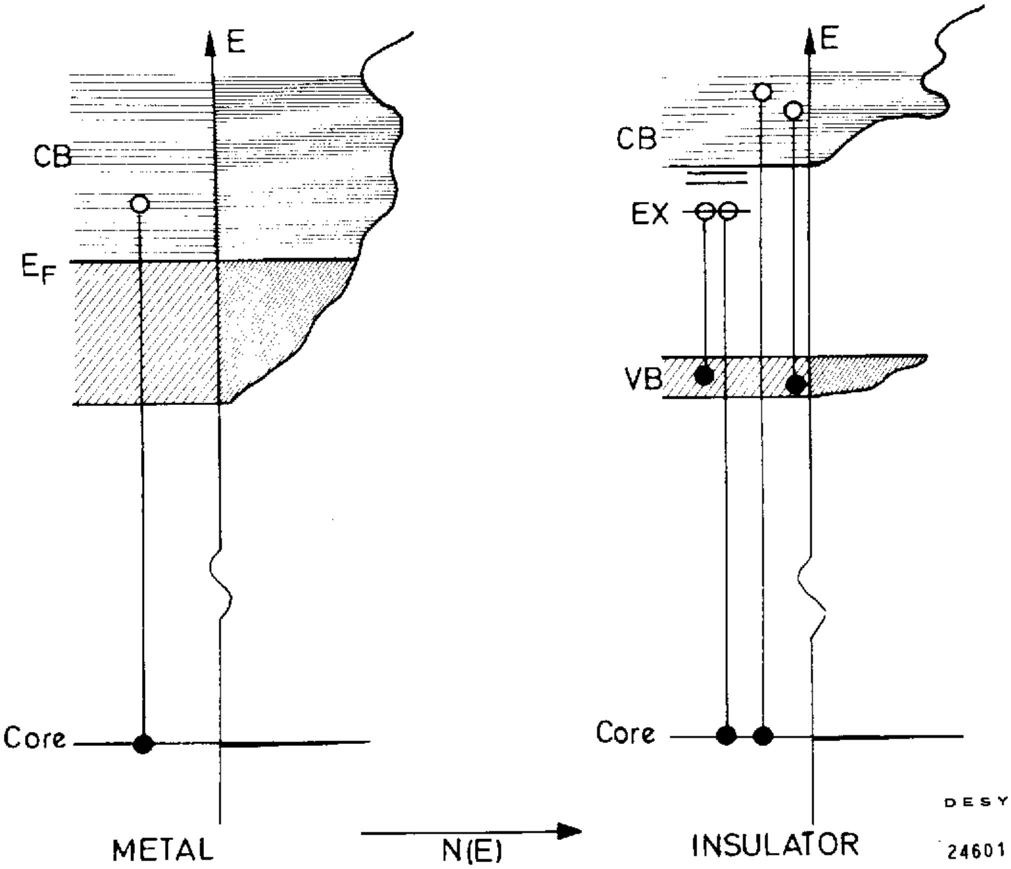

Fig. 1

Fig. 11 Partial yield spectra from a cleaved NaCl (100) crystal surface. The spectra are obtained for polar angles 0^o, 30^o and 60^o and for s and p polarized light. Retarding potentials +15 and −20 V were applied for a variation of the probe depth. This varies from volume sensitivity at +15 V to maximum surface sensitivity at −20 V. Two surface sensitive peaks emerge below the volume 2p core exciton, which corresponds to peaks AB in Fig. 4 (from Ref. 63).

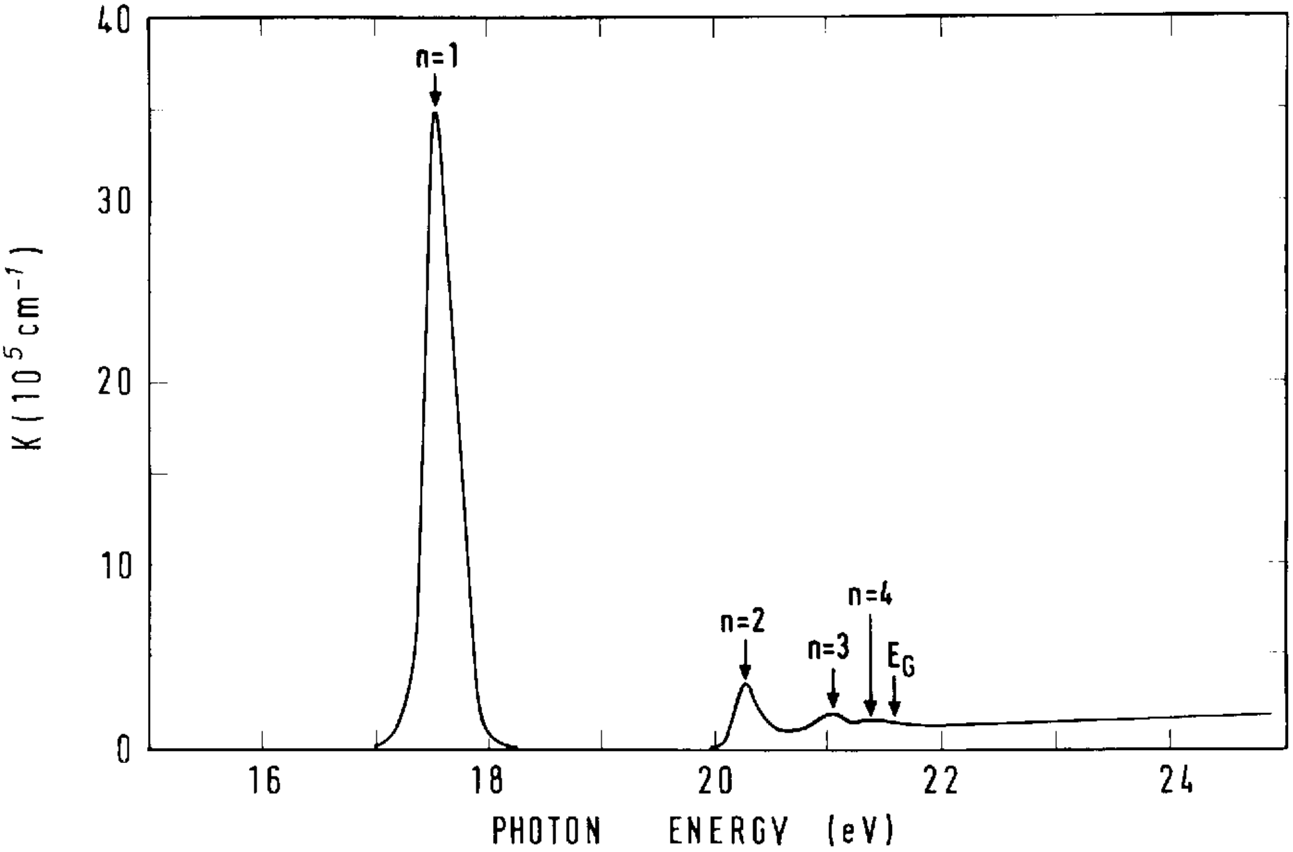
K (10^5 cm^{-1})
40
30
20
10
0
n=1
n=2
n=3
n=4
E_G
16
18
20
22
24
PHOTON ENERGY (eV)

Fig. 2

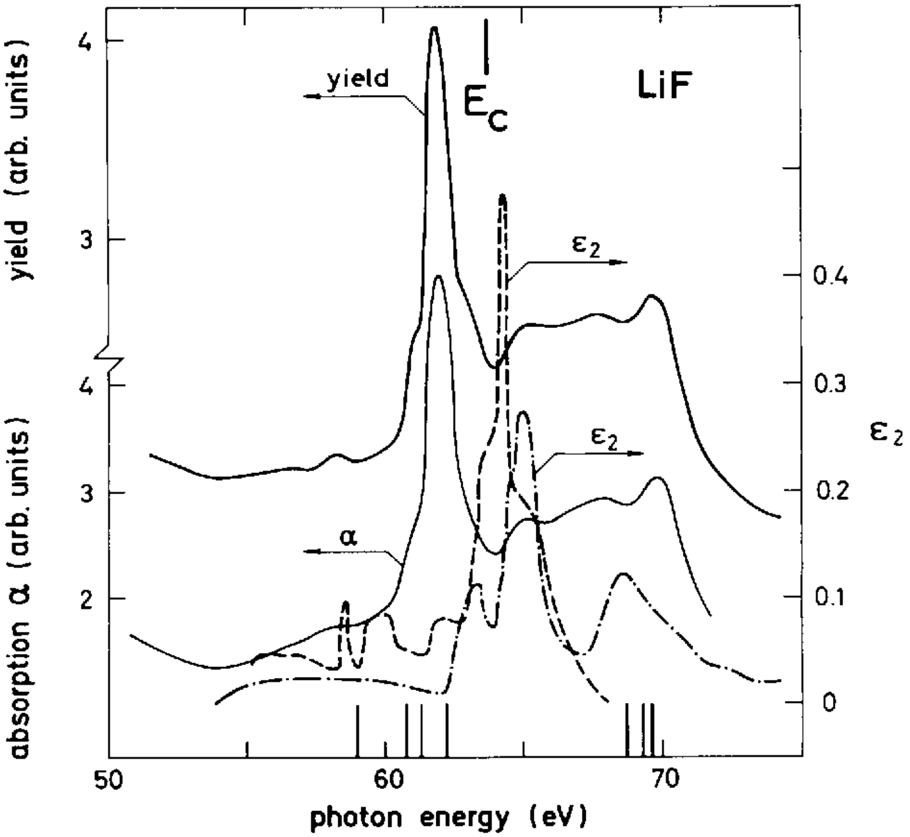
yield (arb. units)
absorption α (arb. units)
4
3
4
3
2
yield
α
E_C
LiF
ε_2
ε_2
ε_2
0.4
0.3
0.2
0.1
0
50
60
70
photon energy (eV)

Fig. 3

DESY

26151

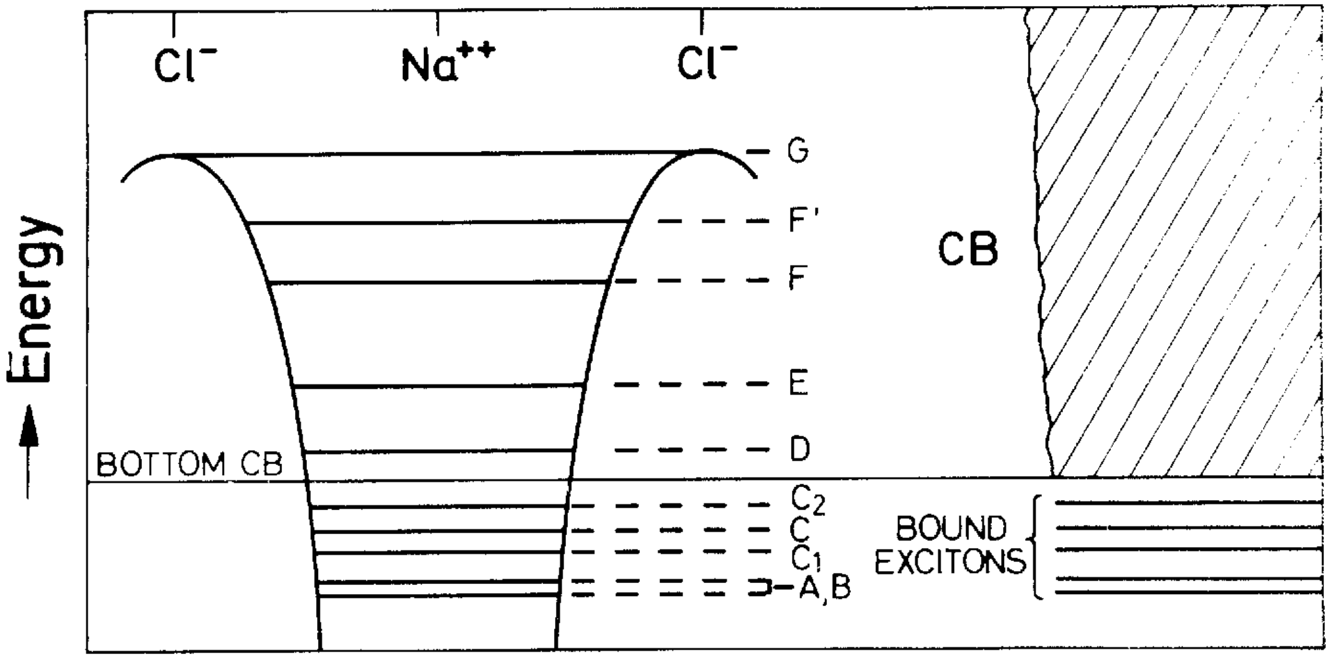

Fig. 5

DESY

26085

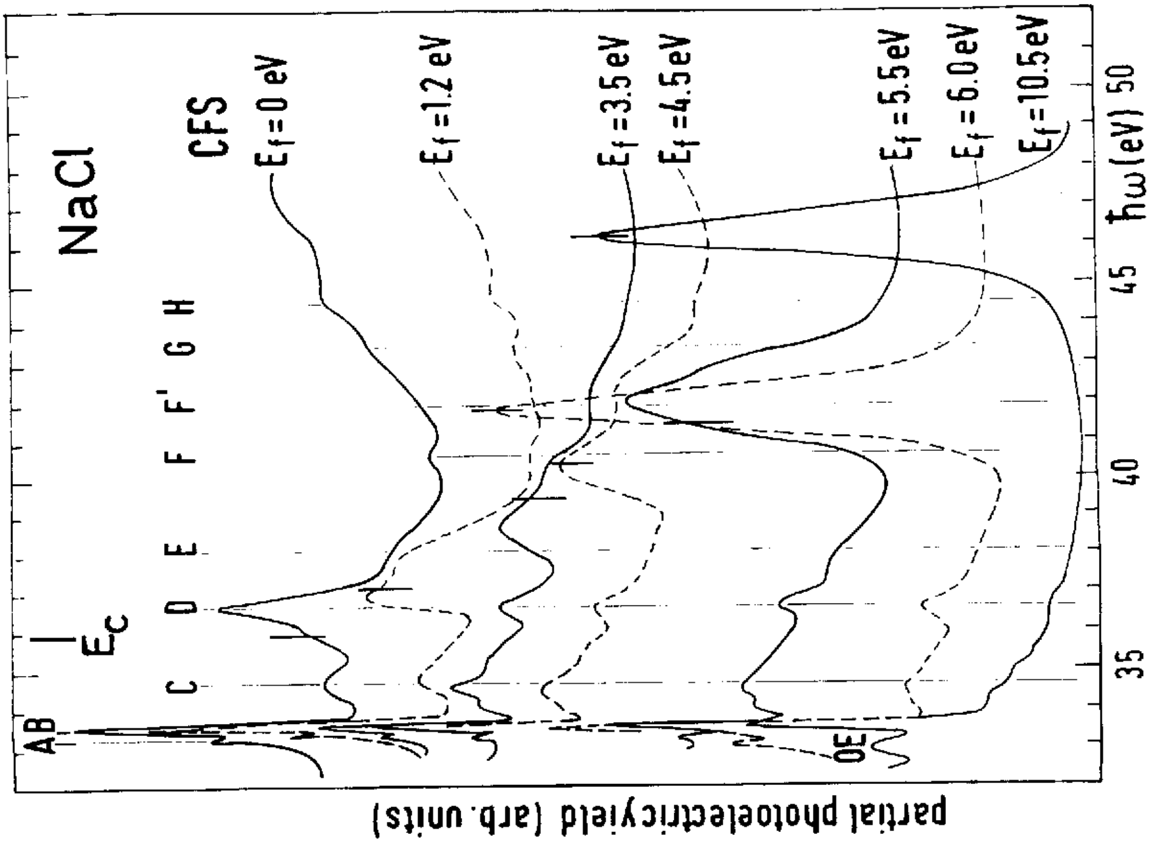

Fig. 4

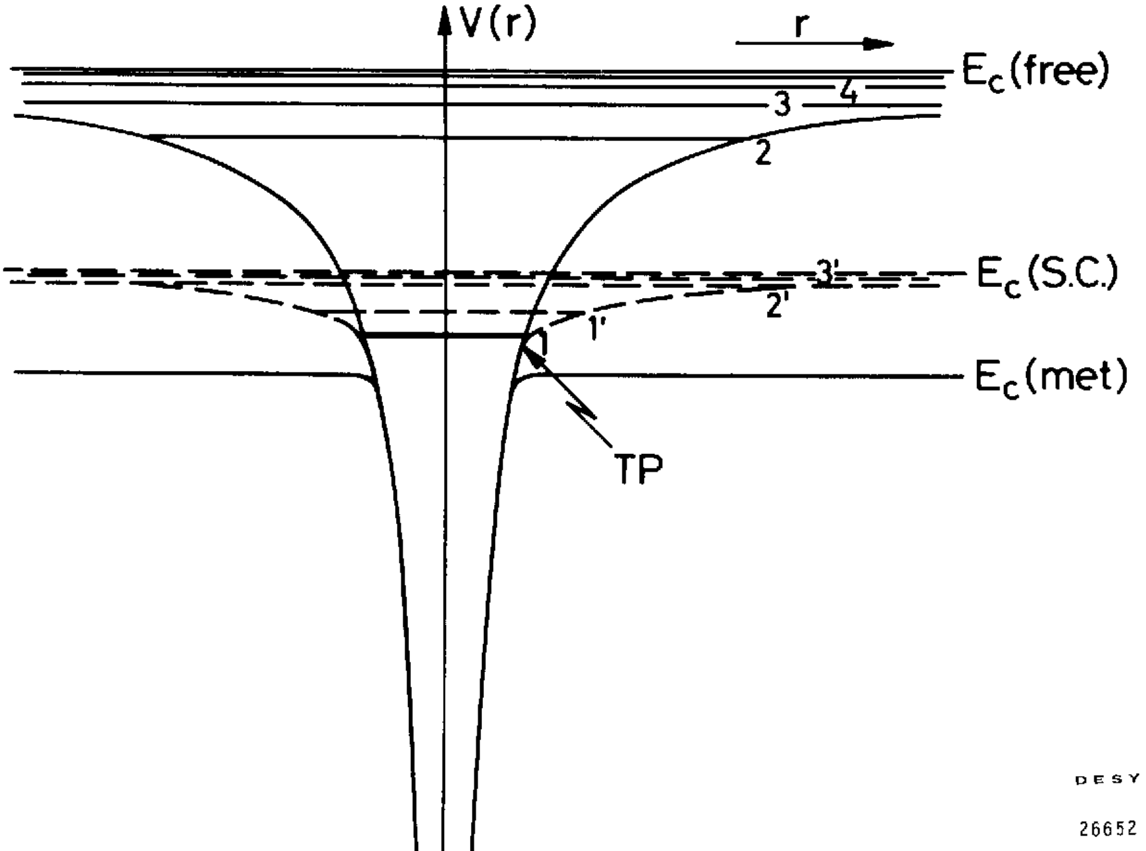
V(r)
r
E_c(free)
4
3
2
E_c(S.C.)
3'
2'
1'
E_c(met)
TP
DESY
26652

Fig. 6

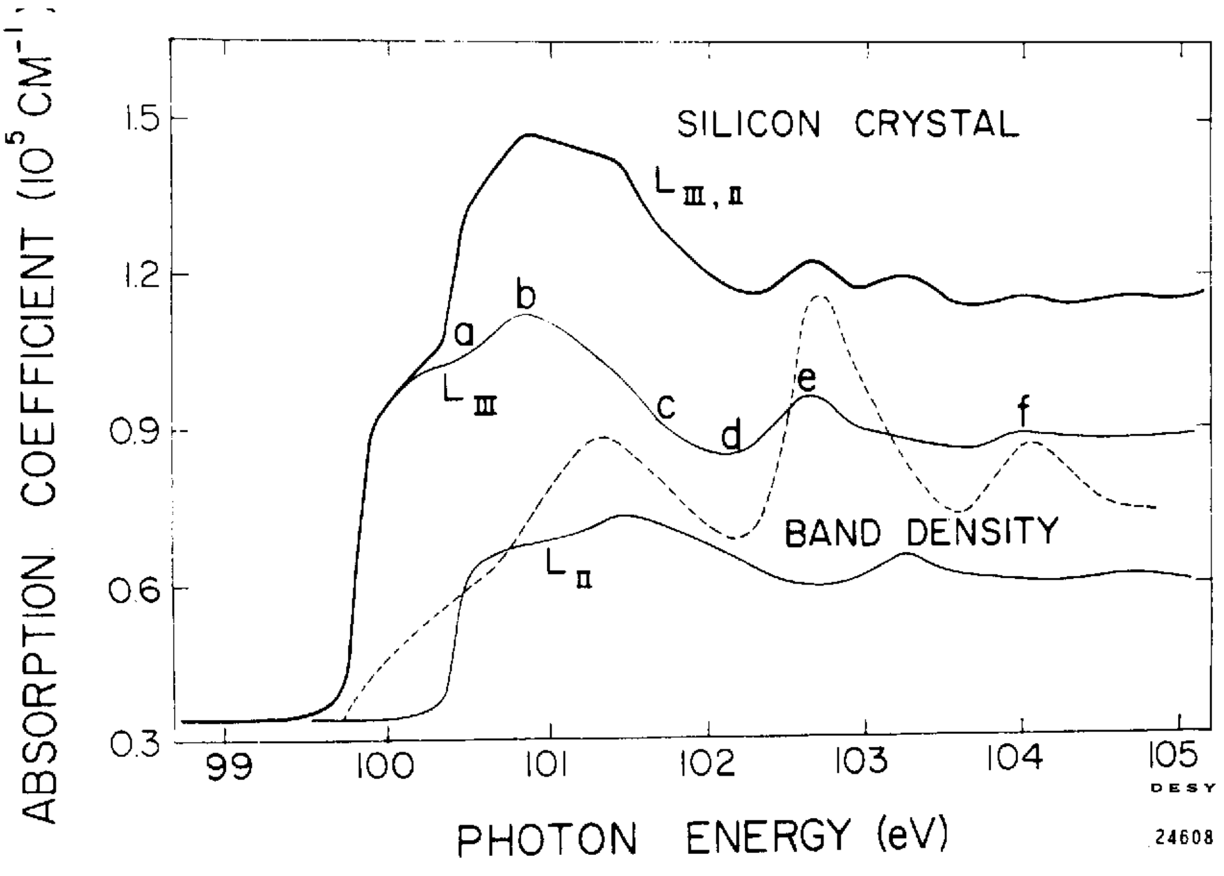
ABSORPTION COEFFICIENT (10^5 CM^-1)
1.5
1.2
0.9
0.6
0.3
SILICON CRYSTAL
L_III,II
a
b
L_III
c
d
e
f
BAND DENSITY
L_II
99
100
101
102
103
104
105
PHOTON ENERGY (eV)
DESY
24608

Fig. 7

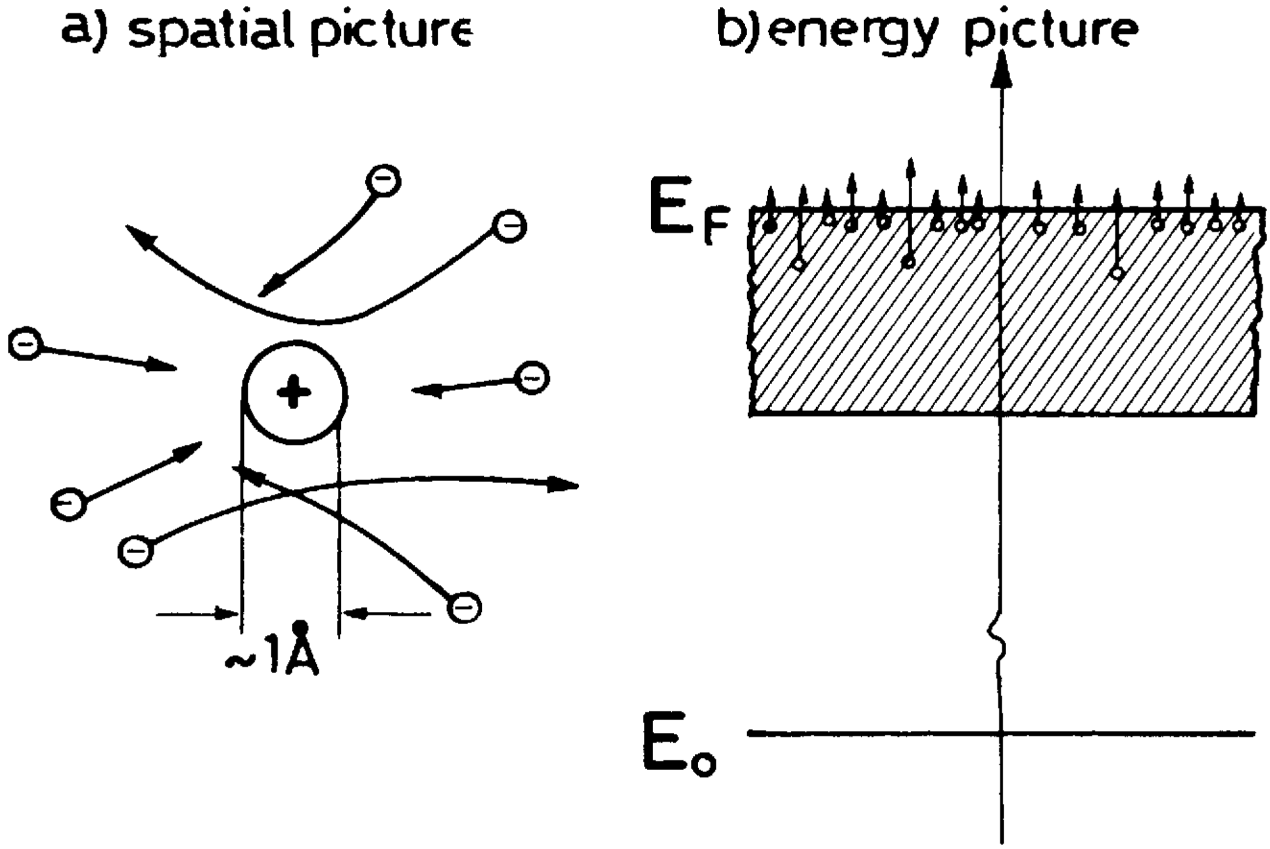
a) spatial picture
b) energy picture
+
~1Å
E_F
E_0

Fig. 8

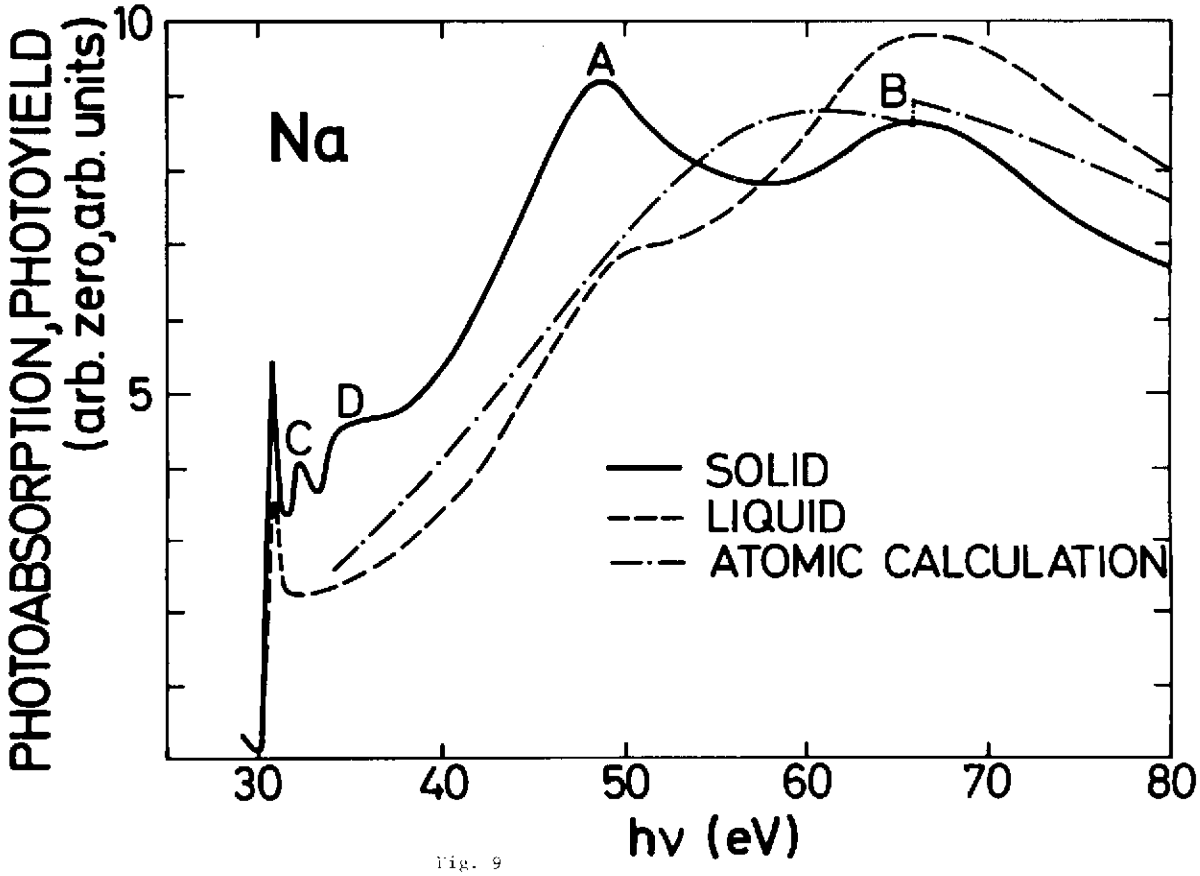
PHOTOABSORPTION, PHOTOYIELD
(arb. zero, arb. units)
10
5
Na
A
B
C
D
SOLID
LIQUID
ATOMIC CALCULATION
30
40
50
60
70
80
hν (eV)

Fig. 9

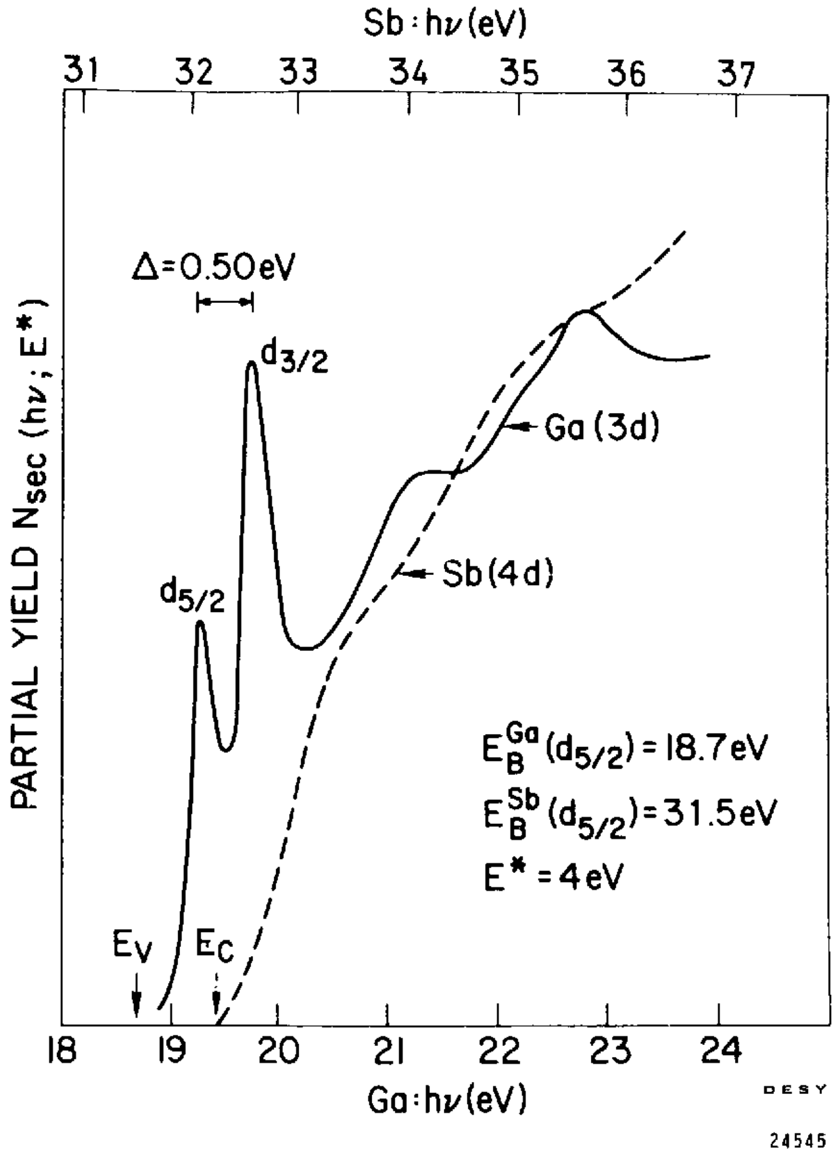
Sb: hν (eV)
31
32
33
34
35
36
37
Δ=0.50eV
$d_{3/2}$
$d_{5/2}$
Ga (3d)
Sb (4d)
$E_B^{Ga}(d_{5/2}) = 18.7eV$
$E_B^{Sb}(d_{5/2}) = 31.5eV$
$E^* = 4eV$
E_V
E_C
PARTIAL YIELD N_{sec} (hν; E*)
18
19
20
21
22
23
24
Ga: hν (eV)
DESY
24545

Fig. 10

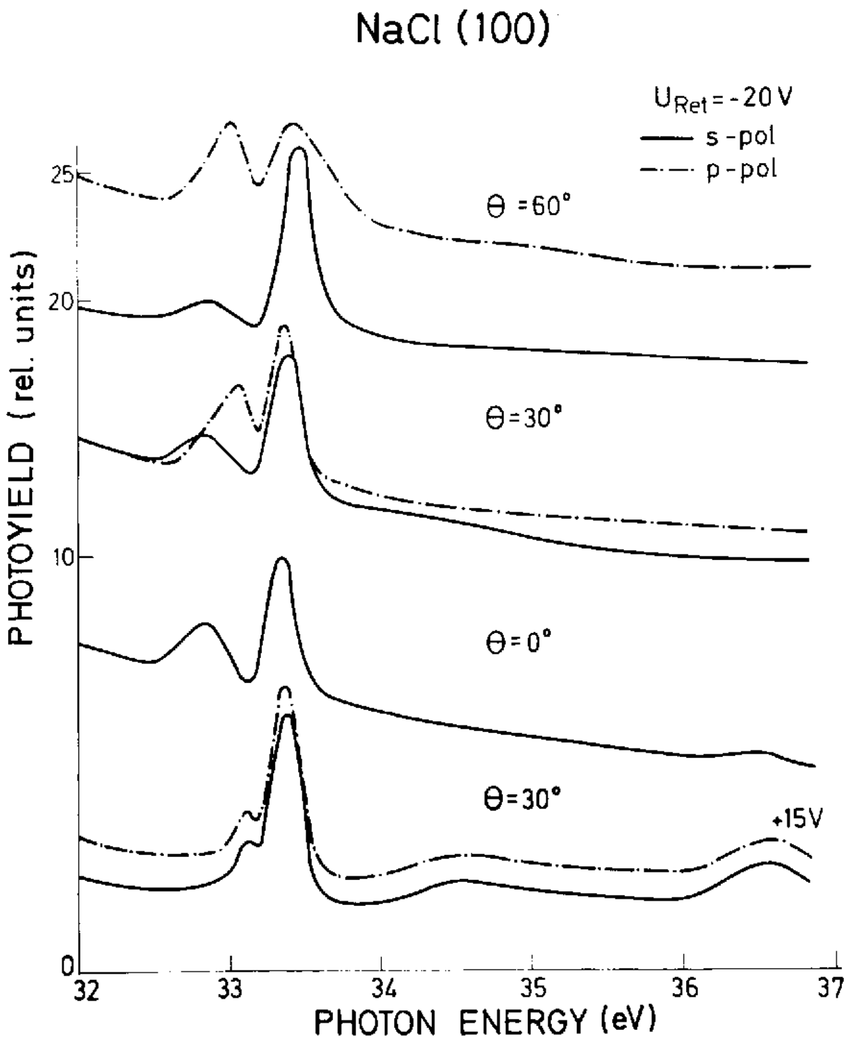
NaCl (100)
U_{Ret} = -20 V
s-pol
p-pol
θ =60°
θ=30°
θ=0°
θ=30°
+15V
PHOTOYIELD (rel. units)
0
10
20
25
32
33
34
35
36
37
PHOTON ENERGY (eV)

Fig. 11