

Photoemission Investigation of Autoionizing Na^+-2p Core Excitons in NaCl

by

M. Iwan

II. Institut für Experimentalphysik, Universität Hamburg

C. Kunz

Deutsches Elektronen-Synchrotron DESY, Hamburg

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

DESY
Bibliothek
Notkestraße 85
2 Hamburg 52
Germany

Photoemission Investigation of Autoionizing Na^+-2p Core Excitons in NaCl

M. Iwan^(a) and C. Kunz^(b)

(a) II. Institut für Experimentalphysik, Universität Hamburg, Luruper Chausse 149,
D-2000 Hamburg 50

(b) Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, D-2000 Hamburg 52

The first sharp structures in the NaCl Na^+-2p absorption spectrum were investigated by means of constant final state spectroscopy (CFS). This method allows for a detailed observation of lattice relaxation and electronic decay processes. The analysis of the spectra leads to an identification of the first ten structures in the absorption spectra as being bound or quasi bound electron hole states. Five of them overlap with the continuum states above the bottom of the conduction band. The latter ones are short lived and autoionize through one electron valence band excitations.

1. Introduction

The optical properties of the alkali halides in the vacuum ultraviolet are the subject of many experimental and theoretical investigations (e.g. Lipari and Kunz 1971, Brown et al. 1970, Haensel et al. 1968). Figure 1 shows the NaCl absorption coefficient (after Haensel et al. 1968) in the region of Na^+-2p excitations and the density of conduction band states (after Lipari and Kunz, 1971). The Na^+-2p transitions set in with a series of several pronounced sharp structures at 33 eV. Because of the close coincidence between the spin-orbit split doublet A,B (Fig. 1) at 33.23 and 33.48 with the first allowed excitations in atomic Na^+ at 32.9 and 33.3 eV (Moor 1949) these lines are considered to be core-excitons of the Frenkel type. Attempts were made to describe the rest of the structure as density of states peaks in terms of a band scheme (e.g. Lipari and Kunz 1971). Because core levels are flat dispersionless bands the density of states of the conduction band should be reflected in the absorption spectrum, neglecting matrix elements. It was also suspected that the structures following A,B could be influenced or even created by the electron hole interaction (Haensel et al. 1968, Nakai et al. 1969 and 1971). Especially Åberg and Dehmer (1973) tried to explain these peaks in terms of resonances inside a potential well at the Na^{2+} -ion which has a potential wall built around it due to the repulsion of electrons from the neighboring Cl^- -ions arising from the Pauli principle (Fig. 2). This led them to a classification of the peaks up to D (Fig. 1) in terms of inner well states having the correct symmetry determined by the octahedral arrangement of the Cl^- -ions. A quantitative treatment of this model, however, would be possible only if the exact potential was known.

A method providing information on the electron hole binding energy independent of theoretical models is to combine absorption spectra in the fundamental range with photoemission measurements. The optical data give the gap energy E_g between the top of the valence band and the bottom of the conduction band, the photo-

electron energy distribution curves (EDC's) give the absolute energy separation between core levels and the top of the valence band if the photon energy is high enough to ionize the core electrons. Such an analysis allows to mark the position of the bottom of the conduction band in the spectrum Fig. 1. The same analysis was carried out by Gudat et al. (1974) for LiF and later by Pantelides and Brown (1974) and Pantelides (1975) for a series of alkali halides. Pantelides (1975) locates the bottom of the conduction band of NaCl at 36.0 ± 0.5 eV taking XPS values for the separation between the top of the valence band and the Na^+2p level.

We report here on an investigation of the sharp structures A to G in Fig. 1 by means of constant final state spectra (CFS) and EDC's making use of synchrotron radiation from the 7.5 GeV synchrotron DESY. The details of the techniques are described in section 2. CFS turn out to be a means to obtain information on the origin of these peaks. The results are described and discussed in section 3.

2. Experimental details

Synchrotron radiation was monochromatized by a specially designed grazing incidence monochromator with a fixed exit beam and an energy resolution of about 400 (Dietrich and Kunz 1972). The angle of incidence at the sample was 45° . The photoemitted electrons of NaCl were measured using an electrostatic energy analyzer of the spherical type and a channeltron multiplier. Thus we had the possibility to measure EDC's (scanning the potential at the sample relative to the entrance slit of the analyzer while the transmission energy of the analyzer and the photon energy are fixed) and CFS's (varying the photon energy continuously while the potential at the sample and the transmission energy of the analyzer are fixed). The latter technique is only possible with a continuous and structureless light source like synchrotron radiation. The joint resolution of the monochromator

and the analyzer was about 0.3 eV at a transmission energy of 30 eV. This was tested with the photoemission lines of the $\text{Al}2p$ levels.

The samples were thin films in the thickness range 20 - 250 Å which were evaporated in UHV with a base pressure in the 10^{-10} Torr range onto substrate layers of evaporated clean Al films. During evaporation the pressure rose into the 10^{-9} Torr range. The film thickness and the evaporation rate were controlled with a quartz crystal thin film monitor (Edwards).

For all NaCl films charging at room temperature was negligible. This was tested by reducing the intensity of the incident light and extrapolating to zero intensity. While all results presented in this paper were performed at room temperature we have also performed in this context measurements at temperatures between 80 and 500 K. We note that at 80 K considerable charging occurred with the thicker films (Lwan and Kunz, 1977).

3. Results and Discussion

As mentioned in the introduction a combination of absorption spectra in the fundamental range with photoemission measurements allows for a determination of the position of the bottom of the conduction band relative to the Na^+2p level. We made UPS measurements to obtain the separation between the top of the valence band and the 2p levels. We have obtained 27.3 ± 0.2 eV for this separation from EDC's like the one shown in Fig. 3. The separation is in agreement with the value of 27.03 eV given by Kowalczyk et al. (1974). Our result does not depend on photon energy in the region 45 - 100 eV, also not on film thickness. Combining our result with the value for the band gap of 8.6 eV as given by Eby et al. (1959)

(a large number of values are collected by Strehlow and Cook, 1973) we obtain 35.9 ± 0.3 eV for the bottom of the conduction band relative to the $\text{Na}^+ - 2p$ level. This is in good agreement with the value of Pantelides (1975) who gives 36.0 ± 0.5 eV. The theoretical estimate of Åberg and Dehmer (1973) was 35 eV. From this assignment it follows immediately that the peak C is also a bound electron-hole state. This peak C is split into three peaks in our new results (Fig. 4) which is in good agreement with the result of Nakai et al. (1971).

Figure 4 shows constant final state spectra with final states close to the bottom of the conduction band. The parameter is the fixed kinetic energy of the electrons in vacuum. The peaks observed at values $E_f \geq 6$ eV are equivalent to the $\text{Na}^+ - 2p$ lines obtained in an EDC (Fig. 3). The extrapolation to $E_f = 0$ allows for a determination of the electron affinity E_A at the bottom of the conduction band yielding $E_A \approx 0$ eV. The marks indicate the position of the final state channel in the spectra as it is determined by the choice of E_f . In the region $E_f < 6$ eV, where the lines are distorted, the position of the marks is obtained as an extrapolation from the spectra for $E_f \geq 6$ eV.

When inspecting the spectra in Fig. 4 it is recognized that the peaks A to G which occur in the absorption spectrum (Fig. 1) are also showing up in most of the CFS's. It was shown by Gudat and Kunz (1972) that the structures found in absorption spectra show up again in the total photoelectric yield spectra. A CFS can be looked upon as a partial photoelectric yield spectrum and also shows the absorption structures (Eastman 1972). Therefore we observe the excitons A,B and other lines. They have been seen already by Haensel et al. (1969) in a different type of partial yield spectra.

The occurrence of these lines is due to Auger decay of core-hole states and direct recombination of excitons followed by electron-electron scattering to channels with low E_f . The most interesting feature in the spectra of Fig. 4 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 to be seen e.g. 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 in this case at a 1 eV higher energy. In the other spectra the same effect is evident. There may be also contributions due to directly emitted electrons on the sides of these peaks. Further spectra at intermediate values of E_f are given by Iwan (1976).

We now want to discuss this result. The onset of electron-electron scattering cannot be responsible for the behaviour of the spectra in Fig. 4. This means that directly emitted electrons from the $\text{Na}^+ - 2p$ initial state into the conduction band can be scattered into channels which have energies below that of the channel into which the directly emitted electrons are excited. Electron-electron scattering sets in with the excitation of the first fundamental exciton peaking at 8.1 eV if we assume that the results of Crouzberg (1966) for high energy electrons are also valid for electrons of low kinetic energies. The onset is at about 7 eV, therefore electron-electron scattering is possible only for $E_f > 7$ eV. Consequently it cannot be responsible for this process. The pronounced change in the shape of the 2p-line occurs between $E_f = 5.5$ eV and $E_f = 6$ eV. We attribute the states up to $\epsilon_c = 43.5$ eV (structure G) to inner well states as discussed by Åberg and Dehmer (1973). This picture allows for an interpretation of the observed behaviour in the following way: we excite an electron in this region into a resonance-like inner well state for which

there is only a small probability to decay into an extended band state (outer well state). During the relative long lifetime of the inner well state relaxation with the emission of many phonons occurs. When the electron finally escapes it has lost between 0 and 1.5 eV of its initial excitation energy to phonons. We therefore consider the particular behaviour of the CFS spectra at and below $E_f = 6$ eV as a strong evidence for the occurrence of quasi-bound inner-well states. In other words: peaks D - G which correspond to states above the bottom of the conduction band are then due to quasi-bound electron-hole states.

Peak F' is only a small shoulder while the absorption coefficient shows a strong increase in this region of photon energy (Fig. 1). This strong increase can be correlated with an increase in the density of states of the conduction bands. This interpretation is deduced from the fact that there is no reduction of intensity of the directly emitted Na^+2p electrons although above $E_f = 7$ eV electron-electron scattering is possible which will cause a reduction of intensity. This reduction must be compensated by an increase in the density of states. Such an increase is in agreement with the Hartree Fock calculations of Lipari and Kunz, 1971 (Fig. 1). Because of the small oscillator strength of structure F' the $E_f = 6$ eV spectrum is dominated at $h\nu = 41.9$ eV by Na^+2p electrons caused by the increasing density of states while F' dominates the $E_f = 5.5$ eV spectrum. The large width of the peak of directly emitted electrons for $E_f \geq 6$ eV, which is far larger than the instrumental resolution, is due to phonon broadening as investigated by Iwan and Kunz (1977) in a separate publication.

A new structure (OE) emerges in the spectra with $E_f = 6$ eV and $E_f = 10.5$ eV (Fig. 4). This structure OE appears to be due to a surface excitation since

it shows up for kinetic energies at which electron-electron scattering sets in. Further investigations by Rehder et al. (1977) on NaCl single crystals corroborate this interpretation.

Another series of investigations was concerned with the question which of the two considered decay mechanisms, Auger or direct recombination (DR), is mainly responsible for the appearance of peaks A to E in Fig. 4 even if $E_f \geq 4.0$ eV. For this purpose we have measured EDC spectra at various photon energies, three of which are displayed in Fig. 5. The selected photon energies correspond to the excitation of excitons B, D and to an interband excitation. In all three cases a strong contribution due to Auger electrons shows up, which are centered around an energy $E_{kin} + E_{gap} \approx 21$ eV above the top of the valence band. There is, however, a striking difference in the shape between the spectrum excited at the exciton B ($h\nu = 33.48$ eV) and those at the higher photon energies.

This result is not so surprising, since the Auger decay of an isolated core hole and of a bound exciton like B is quite different. We assume that exciton D is autoionizing before the Auger process takes place. While the ordinary Auger process involves two electrons from the valence band, the Auger decay of an exciton involves in addition the electron which is originally bound to the hole. In the case of NaCl the additional charge which is originally centered on the Na^+ ion will move to the Cl^- ions (valence band) during the Auger process. As a consequence the originally bound electron will be expelled into a conduction band state acquiring a certain amount of kinetic energy. The Auger electron distribution is therefore smeared towards lower kinetic energies as it is observed in Fig. 5. A quantitative theory of this problem appears to be very difficult. An

equivalent process in the gas phase, namely Auger decay from excited deep level resonance states in Xe and Kr was recently investigated by Eberhardt et al. (1977).

We have also investigated the direct recombination contribution to the decay process. For this purpose we have measured the CFS spectra at very high values of E_f namely $E_f = 18$ eV and $E_f = 20$ eV as shown in Fig. 6. The highest possible energy for Auger electrons is $E_f = 17.6 \pm 0.5$ eV (26.2 eV above the top of the valence band) while direct recombination yields electrons at energies up to the exciton energy above the top of the valence band (e.g. 36.60 eV for exciton D). The CFS spectrum at $E_f = 20$ eV ($\Delta E = 1$ eV) therefore demonstrates that excitons B to D can undergo direct recombination. Because of the finite resolution $\Delta E = 1$ eV the other structures in the $E_f = 18$ eV spectrum might arise from Auger decay. It is interesting to note that the surface excitation OE also decays by direct recombination.

Direct recombination was first discussed for NaCl by Haensel et al. (1969) and later verified for several potassium halides by Blechschmidt et al. (1970). Lapeyre et al. (1974) were the first to use constant initial state (CIS) spectra to prove the presence of this process in KI. They give a relative probability of the Auger to the direct recombination channels as two to one. In order to obtain this result several assumptions on attenuation lengths due to inelastic scattering processes had to be made the errors of which are difficult to estimate. We therefore refrain from a similar evaluation of this ratio.

Conclusions

Our results lead us to conclude that the peaks A, B, C₁, C, C₂ in the spectra (Fig. 1,4) of NaCl are due to excitons of the Frenkel type below the bottom of the conduction band. Further peaks D - G correspond to states above the bottom of the conduction band and are due to quasi-bound inner-well states according to the considerations given above. We do not believe that an alternative interpretation of our results which is founded completely on the one electron band picture is consistently possible. An attempt of such an interpretation would involve energy loss of the excited electron due to electron phonon scattering on its way out of the crystal. This would in principle explain the reduction of electron energy as it was observed above. This model would, however, not explain a threshold of this process between 5.5 and 6 eV. The threshold would rather be expected to occur above $E_f = 7$ eV. Further, the electron-phonon scattering mean free path as calculated by Llacer and Garwin (1969) in NaCl is 30 Å for $E_f = 3$ eV. The thickness of the film for which we have discussed our results is only 70 Å. It would not allow for a long enough path of the escaping electrons to undergo an energy loss of more than 1 eV. In addition, some of our measurements were taken with even thinner samples (down to 20 Å) yielding essentially the same results. This leads us to a rejection of such a mechanism for the interpretation of our measurements.

- Åberg T., Dehmer J.L., 1973, J.Phys. C6, 1450
- Blechschmidt D., Skibowski M., Steinmann W., 1970, Opt.Comm. 1, 275
- Brown F.C., Gähwiller C., Fujita H., Kunz A.B., Scheifly W., Carrera N., 1969, Phys.Rev. B2, 2126
- Creuzburg M., 1966, Z. Physik 194, 211
- Dietrich H., Kunz C., 1972, Rev.Sci.Instr. 43, 434
- Eastman D.E., 1972, Techniques of Metals Research VI, ed. E. Passaglia (Interscience), p. 413
- Eberhardt W., Kalkoffen G., Kunz C., to be published
- Gudat W., Kunz C., 1972, Phys.Rev.Lett. 29, 169
- Gudat W., Kunz C., Petersen H., 1974, Phys.Rev.Lett. 32, 1370
- Haensel R., Kunz C., Sasaki T., Sonntag B., 1968, Phys.Rev.Lett. 20, 1436
- Haensel R., Keitel G., Peters G., Schreiber P., Sonntag B., Kunz C., 1969, Phys.Rev.Lett. 23, 530
- Iwan M., 1976, Diplomarbeit Universität Hamburg and Int.Ber. DESY F41-76/09
- Iwan M., Kunz C., 1977, Phys.Lett. 60A, 345
- Kowalczyk S.R., McFeely F.K., Ley L., Pollak R.A., Shirley D.A., 1974, Phys.Rev. B9, 3573
- Lapeyre G.J., Baer A.D., Hermanson J., Anderson J., Knapp J.A., Gobby P.L., 1974, Sol.Stat.Comm. 15, 1601
- Lapeyre G.J., Anderson J., Knapp J.A., Gobby P.L., Proceedings of the IV Int.Conf. on Vacuum Ultraviolet Radiation Physics, Hamburg (1974), ed by E.E. Koch, R. Haensel and C. Kunz, pp. 380-382
- Lipari N., Kunz A.B., 1971, Phys.Rev. B3, 491
- Llacer J., Garwin E.L., 1969, J.Appl.Phys. 40, 2766 and 2776
- Moore C.E., 1949, NBS-Circular (U.S.) Circ.No. 467, Vol. 1
- Nakai S., Sagawa T., 1969, J.Phys.Soc. Japan 26, 1427

- Nakai S., Ishii T., Sagawa T., 1971, J.Phys.Soc. Japan 30, 428
- Pantelides S.T., 1975, Phys.Rev. B6, 2391
- Pantelides S.T., Brown F.C., 1974, Phys.Rev.Lett. 33, 299
- Rehder U., Gudat W., Hayes R., Kunz C., 1977, Verhandl. DPG (VI) 12, 332 and to be published
- Strehlow W.H., Cook E.L. 1973, J.Phys.Chem.Ref. Data 2, 163

Figure Captions

Fig. 1 The upper part shows the absorption coefficient of NaCl in the region of the Na^+2p excitation (after Haensel et al. 1968).

The lower part shows a calculated density of conduction band states (after Lipari and Kunz 1971). The bottom of the conduction band is shifted to the experimental value.

Fig. 2 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 spectrum of Fig. 1 and the position of these levels anticipates the analysis of the spectra of Fig. 4.

Fig. 3 Energy distribution curve of a 20 \AA NaCl film, at a photon energy of 91 eV. CEL denotes structures due to characteristic energy losses, E_F the Fermi edge. The substrate was a clean Al film.

Fig. 4 Constant final state spectra from a $d = 70 \text{ \AA}$ thick NaCl film. E_F is the final state energy relative to the bottom of the conduction band.

Fig. 5 Low kinetic energy region of EDG's at the excitation energies of the exciton B and D and at 60.05 eV where only an inter-band transition occurs. The spectra are normalized with respect to each other at $E_{\text{kin}} + E_{\text{gap}} = 12.2$ eV. The structure between 20 and 25 eV is generated by Auger decay. The structures up to 18 eV represent density of states structures (see Lapeyre et al. 1974).

Fig. 6 CFS's at final state energies where the Auger decay and direct recombination (DR) channels are separated. The right scale is valid for the upper spectrum (only DR). Both spectra are normalized at the background before the onset of 2p transitions.

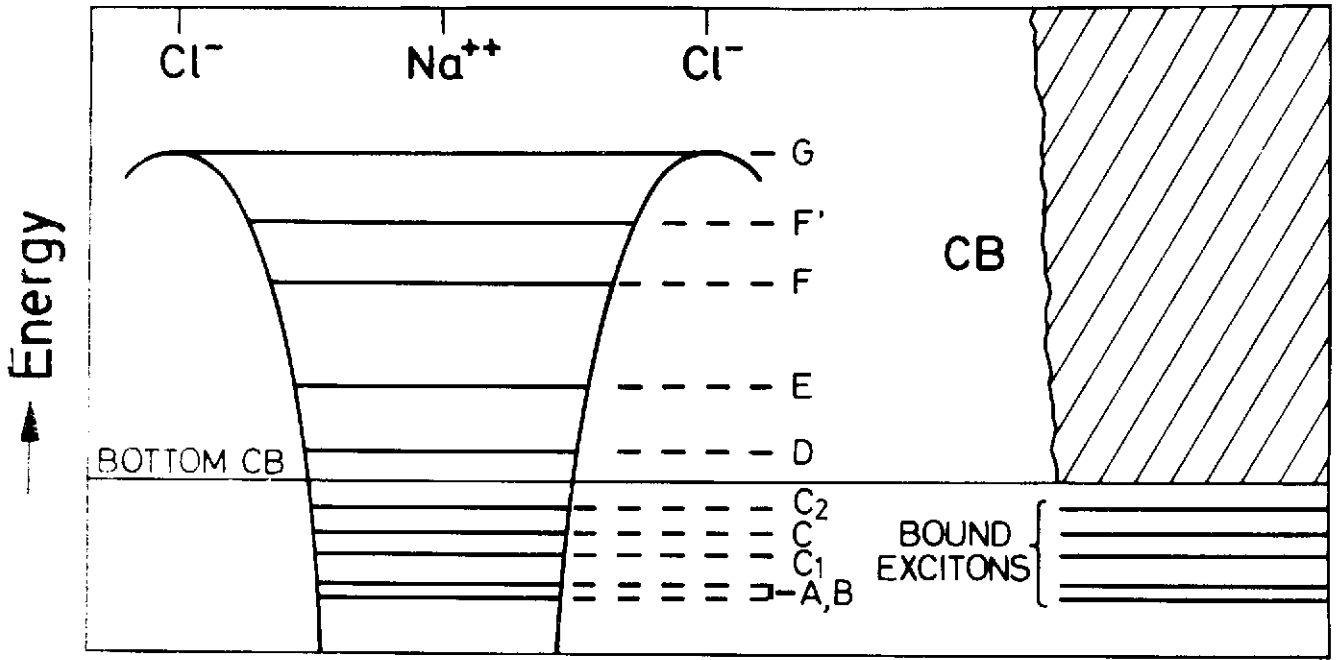


Fig. 2

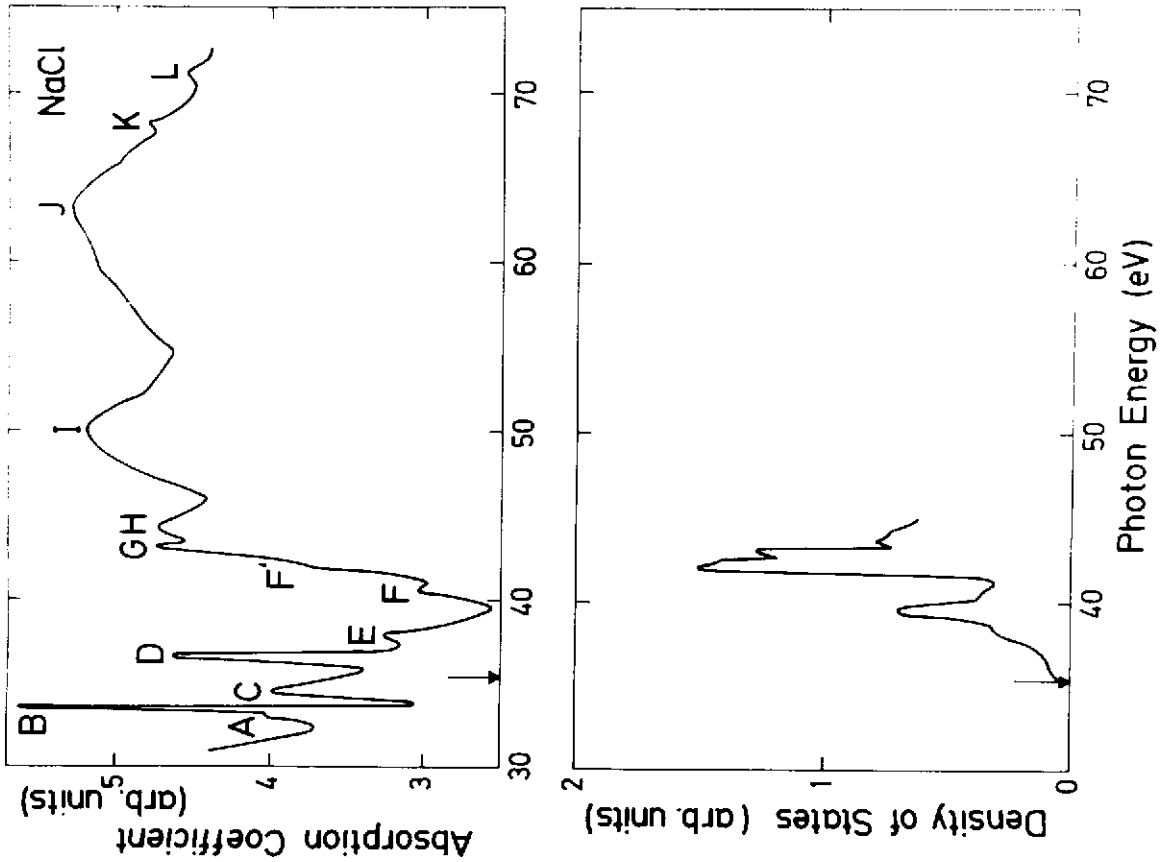


Fig. 1

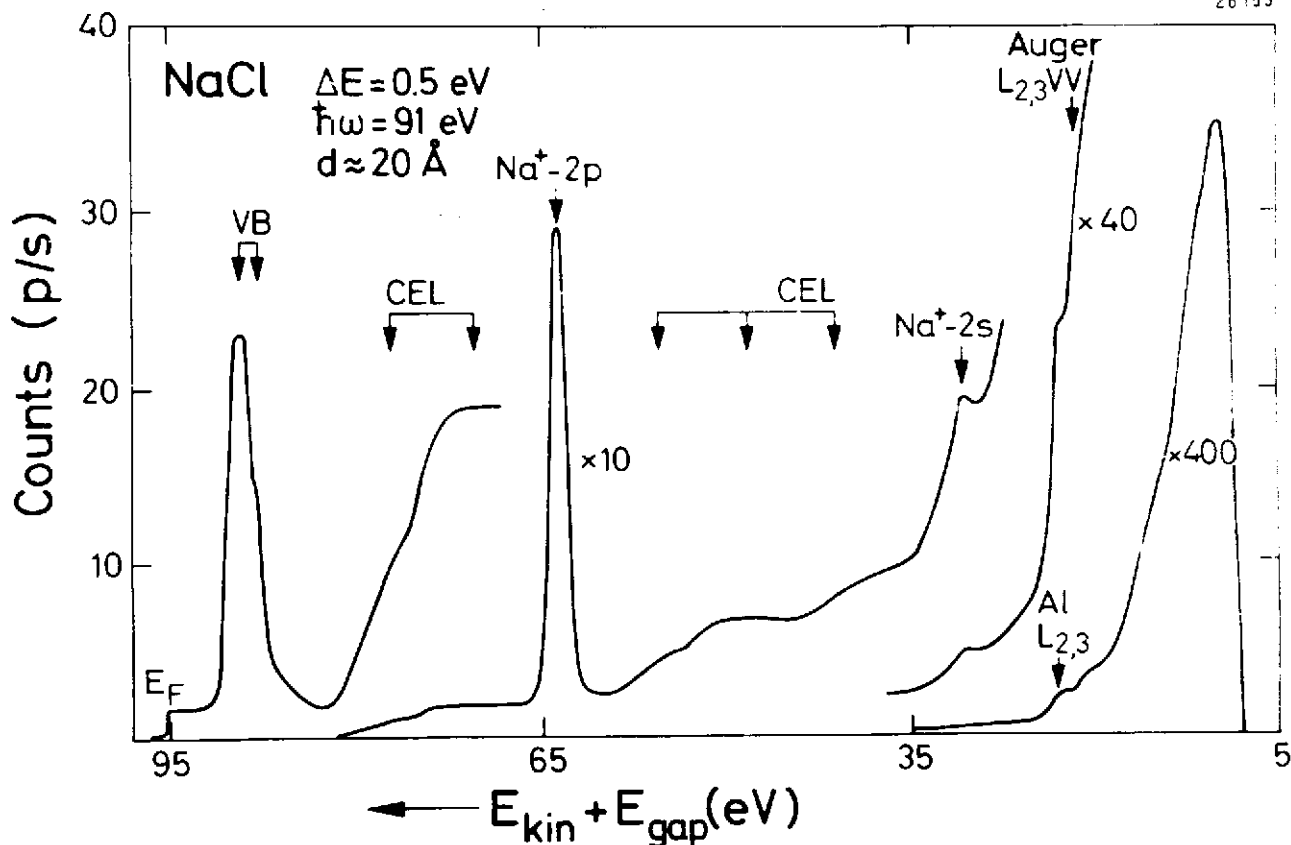
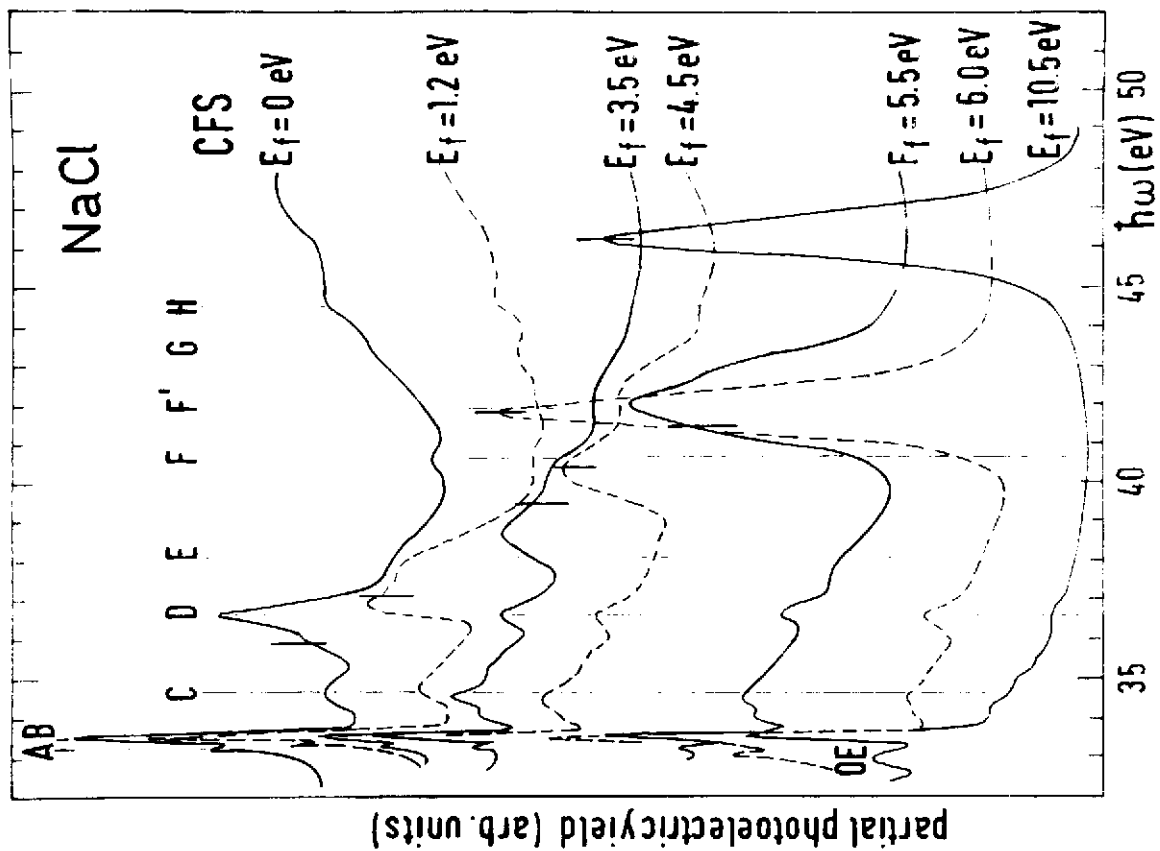


Fig. 3

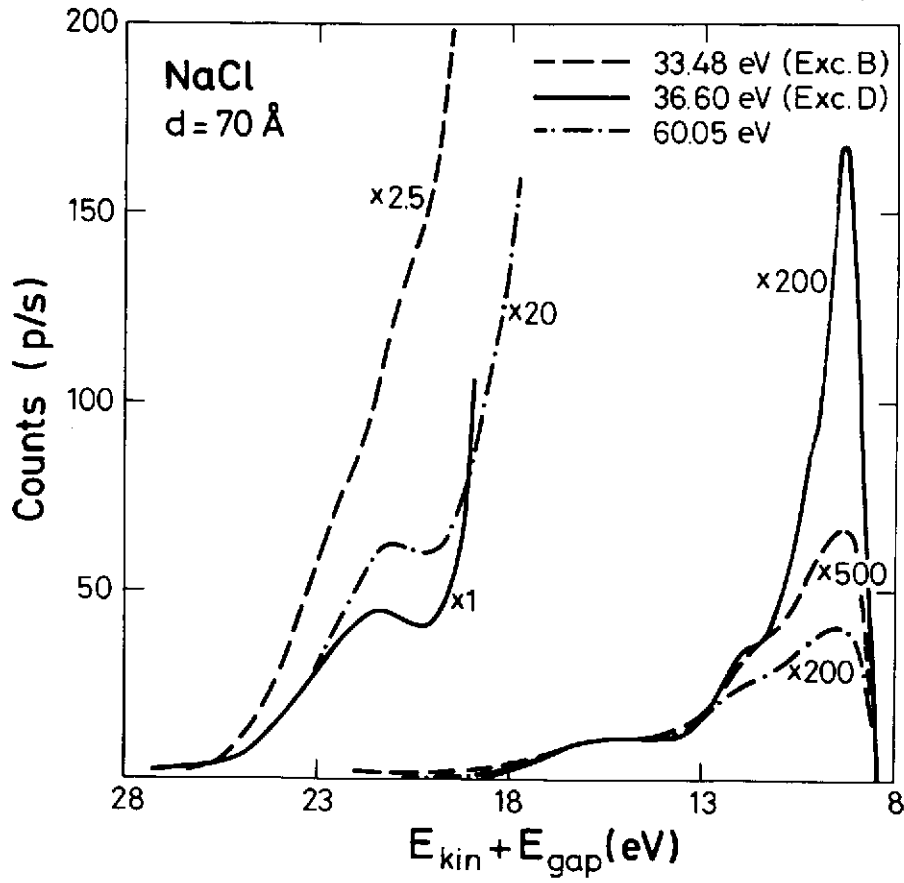


Fig. 5

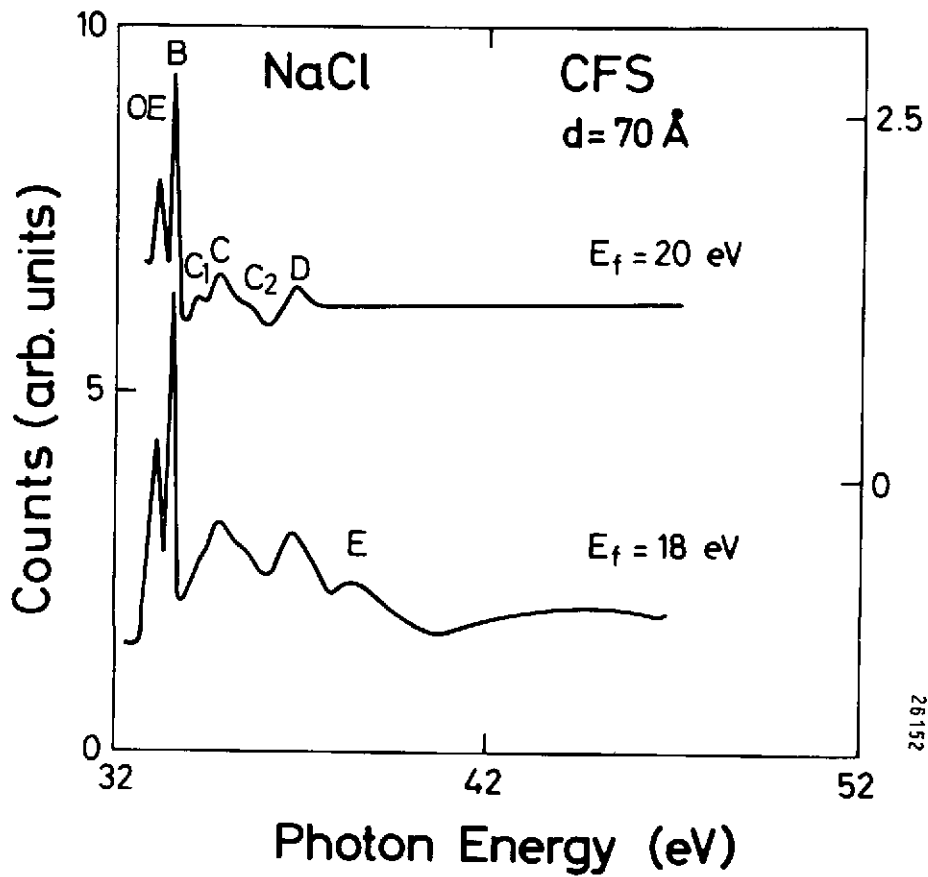


Fig. 6