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Angle and Energy Dependence of Photoemission from NaCl and KCl Single Crystals

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The dependence of the photoemission on the azimuthal emission angle at fixed polar angle of 45° has been measured for the (100) face of NaCl and KCl single crystals cleaved in situ. The initial and final state energy was scanned using the synchrotron radiation of DESY. Strong variations of the angular pattern are observed for different final energies. Below the electron-electron scattering threshold the pattern depends only on the final energy irrespective of whether the level has been populated by direct optical excitation from the valence band or the K^+ *3p core level or by electron-electron-scattering from higher conduction band states. Electron-phonon scattering can account for this fact. The emission in the (110) direction is compared with an existing band structure calculation.*

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Experimental data suitable for testing band structure calculations for alkali halides are remarkably scarce in view of the enormous number of experiments which have been performed with these fundamental compounds. The reason for this is the dominating influence of excitons on the optical spectra and the excellent insulating properties which restricted so far photoelectron spectroscopy to samples of thin evaporated films.

In this letter we report on the first ultraviolet photoemission experiment with bulk alkali halide single crystals. This allows to measure the angular distribution of the photoelectrons, as has been done before with metals and semiconductors[1-7]. Although our investigation was incomplete since the polar angle could not be varied, the data yield considerably more detailed information than former experiments which integrated over all angles. They show that angle resolved photoelectron spectroscopy on alkali halides is possible and may prove to be a promising method of investigating the electronic structure in detail, if the problem of matching the wave functions at the surface can be attacked successfully[8].

We have used the synchrotron radiation of DESY as a light source. This enabled us to vary the photon energy continuously and to scan either the initial or the final state energy of the photoelectrons. The experimental equipment has been described previously[9,10]. It consisted essentially of a normal incidence monochromator with 2 Å resolution and an UHV sample chamber of a base pressure in the 10^{-11} Torr range. NaCl and KCl single crystals were mounted on a rotary motion feedthrough. The axis of rotation coincided with the direction of the incident light. The crystals were cleaved in vacuo, the cleavage plane (100) being normal to the incident light beam. Photoelectrons were analyzed at a constant take off angle of 45° towards the normal of the surface (polar angle).

The emission plane, defined by the emission direction and the normal of the surface, also contained the electric field vector of the incident light. The azimuthal emission angle was varied with respect to the crystal by turning the sample around its normal (see insert Fig. 1). The electron energy analyzer of the filter lens type had an energy resolution of better than 0.2 eV and an angular acceptance of 3^{o}.

A serious problem is posed by the insulating properties of the crystals which result in excessive charging. We have overcome this difficulty by compensating the photoelectron current with thermal electrons from a heated tungsten filament located at a distance of 7 cm in front of the sample. Backscattered compensation electrons formed a peak about 1 eV wide at the bottom of the energy distribution. No background was found for kinetic energies higher than 2 eV. The experimental results proved that spatial and temporal fluctuations of the potential at the photoemitting part of the sample could be kept below 0.5 eV by this compensation.

Residual magnetic fields were held below 50 mG by Mu-metal shielding. Additionally applied fields of the magnitude of the ambient earth field did not change the shape of the angular patterns. For electron energies below 5 eV at most an angular offset of a few degrees and an overall decrease of the intensity could be detected. This can be explained by the limited angular acceptance of the analyzer combined with the size of the illuminated spot and the sample-to-analyzer distance. It ensures that any electron that has been deflected appreciably is not registered. The arrangement was tested for possible artifacts in the azimuthal photoemission pattern with a piece of glass as a sample. No variation of the intensity with azimuthal angle was detected in this test.

Examples of the azimuthal patterns from KCl at fixed electron energies are given in Fig. 1. Pronounced changes of the pattern with photon energy are observed. Note that photoemission from the K^+3p core level yields the same pattern as from the Cl^-3p valence band if the final state electron energy is the same. This holds also for different initial states within the valence band, as is shown in Fig. 2 for a restricted set of data from NaCl: A change of 0.5 eV in the initial energy does not produce any noticeable difference in the azimuth pattern while the same change in the final energy inverts the minimum in the 10-direction. Within the limits of our resolution we have found that the NaCl angular pattern depends only on the final energy in the whole range below 19 eV. For higher energies, however, the pattern shows a significant dependence on both initial and final state energy.

This behaviour can be explained by electron-phonon-scattering below the onset of electron-electron-scattering at final energies exceeding twice the band gap energy E_g ($E_g \approx 8.5$ eV for NaCl[13]). Below this threshold the escape depth of the photoelectrons is large compared to the electron-phonon scattering length. This leads to an extraordinarily high photoelectric yield exceeding 0.5 electrons per photon[11] which has been explained by random walk. Consequently a photoelectron escaping from the sample has undergone several phonon scattering processes and lost completely the correlation to its initial position in k-space. The angular distribution is determined by the density of final states. Above the electron-electron-scattering threshold the escape depth decreases within a few eV to values smaller than the electron-phonon-scattering length[12]. The number of high energy photoelectrons is drastically reduced, but those which escape have not been scattered by either electrons or phonons. Their directions of emission depend on the k-vector of the initial state even though the situation is complicated by the fact that

at most the component of the k-vector parallel to the surface is conserved during the escape.

Most of the electrons excited to these high final state energies will undergo electron-electron-scattering before they reach the surface, thereby loosing an amount of energy $E_s \gtrsim E_g$ and populating conduction band states of energy $E'_f = E_f - E_s$. We have found that the azimuthal pattern of these scattered electrons is the same as that of the valence electrons excited directly to the final state energy E'_f.

In Fig. 3 is shown how the azimuthal pattern changes with final state energy over the range investigated. The data contain the relevant information about the density of final states 4 - 13 eV above the bottom of the conduction band corresponding to the angles of emission. In general, the relation between Bloch states in the crystal and a plane wave outside has to be established by matching the wavefunctions at the boundary. This is a problem similar to the one encountered in LEED-intensity calculations. A solution requires some foreknowledge of the conduction band states and wavefunctions. Nearly free electron models[15] may fail to give a complete description because of the d-bands. If one neglects these complications and tries a rather crude approximation, assuming that the k-direction in the crystal is the same as outside one can compare the variation of the intensity in, e.g., the (10) direction with the density of states along the Σ-axis. As can be seen in Fig. 3, there is a maximum in the (10) direction up to a final state energy of 16 eV which changes into a minimum between 18 and 20 eV. This behaviour can be accounted for by a band structure calculation[14] which shows along the Σ-axis a region with high density of flat bands up to 16 eV and the onset of a parabolic band

at 17 eV. - The investigation of valence band states is possible by studying the angular distributions at final energies above 20 eV where the results depend also on the initial states.

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Figure Captions:

Fig. 1: Polar diagram of the photoemission intensity I as a function of azimuth ϕ for the KCl (100) face at fixed polar angle θ of 45° for three final energies (15, 16 and 18 eV above the top of the valence band) and two initial energies (Cl^- 3p valence band and K^+ 3p core level). (10) marks the orientation in which the (10) surface vector lies in the emission plane.

Fig. 2: Dependence of photocurrent on azimuth for the NaCl (100) face for two initial energies E_i in the valence band and two final state energies E_f. The zero line of the central curve is the bottom of the frame. The zero line of the higher and lower curve has been shifted for clarity reasons.

Fig. 3: Azimuthal patterns of the valence band photoemission from a NaCl (100) face. The zero line is shifted proportional to the final state energy as indicated on the right hand side of the figure. The curves are normalized with respect to their maximum value.

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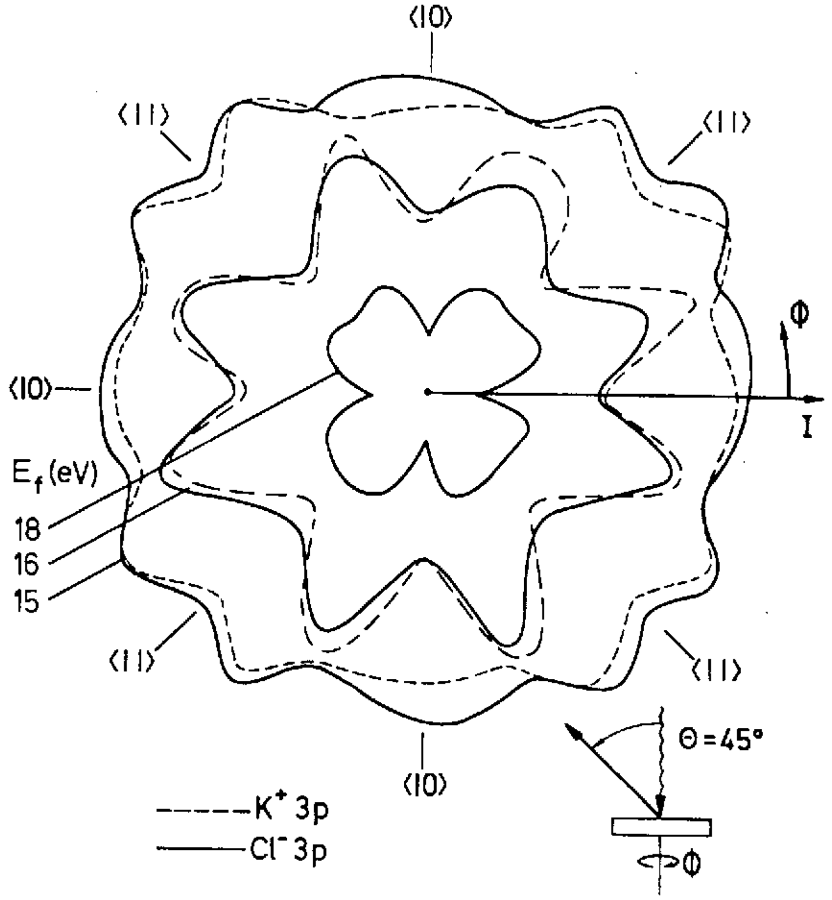

Fig. 1

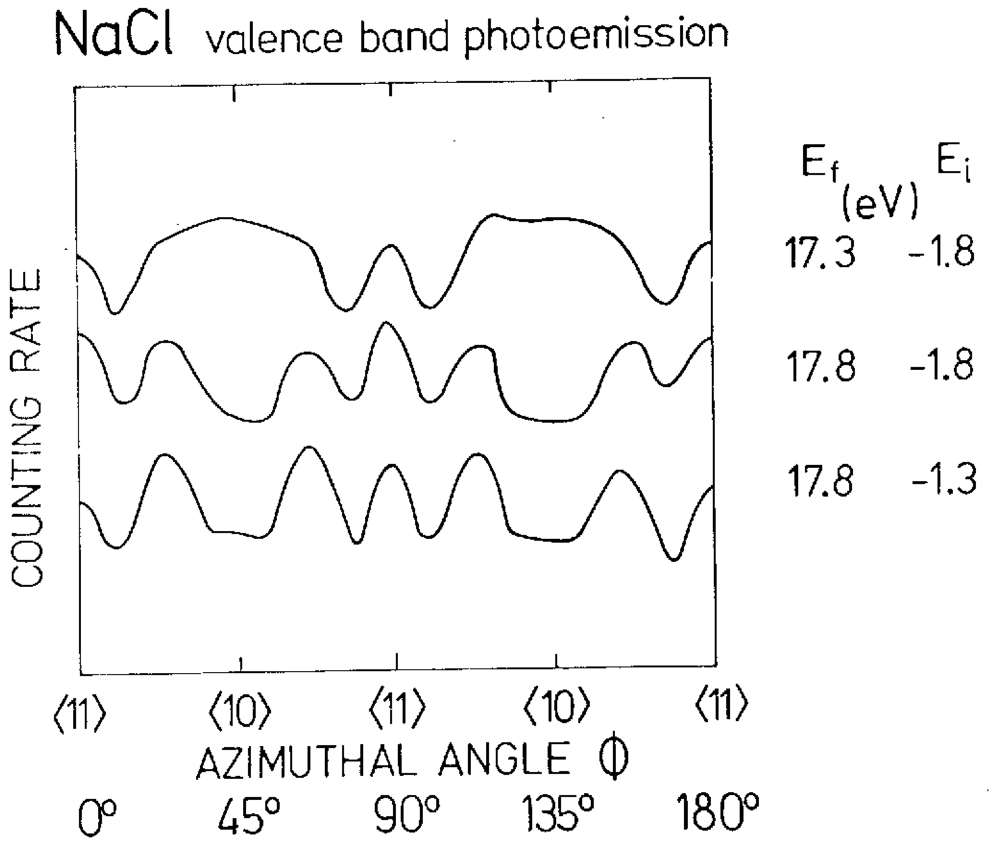
NaCl valence band photoemission
COUNTING RATE
E_f (eV) E_i
17.3 -1.8
17.8 -1.8
17.8 -1.3
⟨11⟩
⟨10⟩
⟨11⟩
⟨10⟩
⟨11⟩
AZIMUTHAL ANGLE Φ
0°
45°
90°
135°
180°

Fig. 2

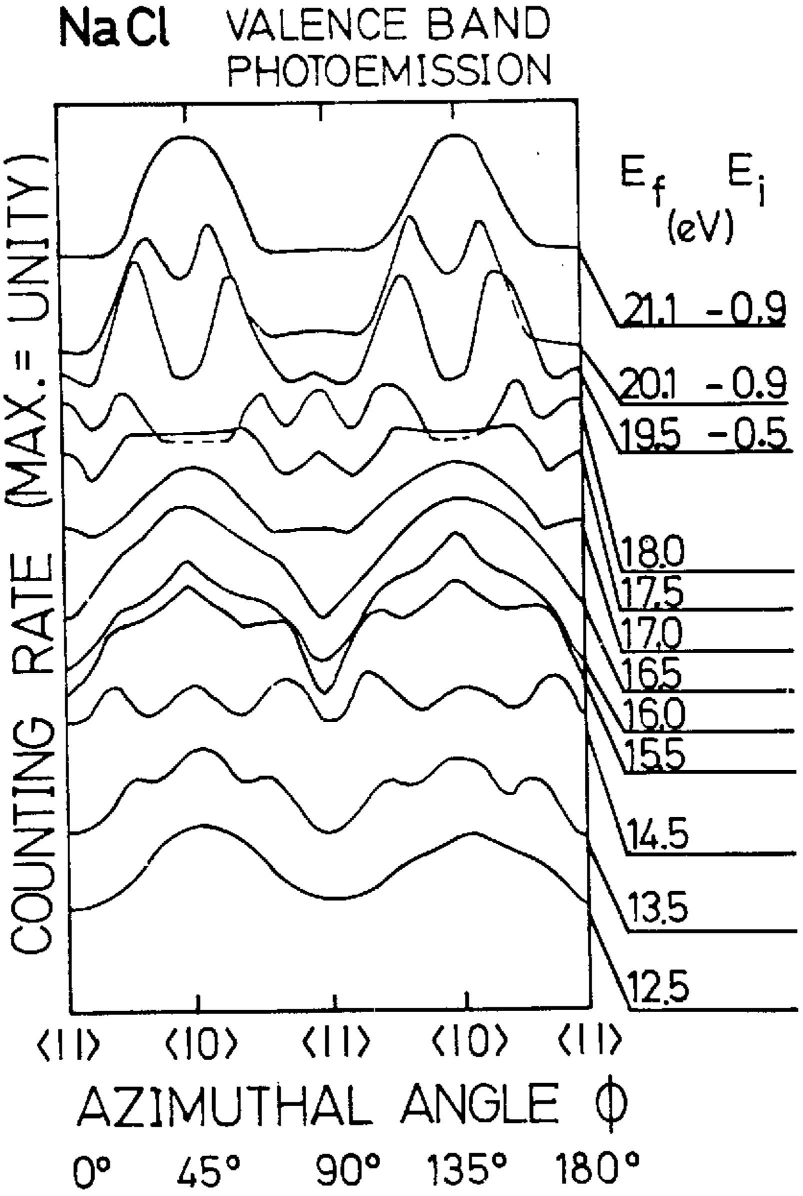
NaCl VALENCE BAND PHOTOEMISSION
COUNTING RATE (MAX.= UNITY)
E_f E_i (eV)
21.1 -0.9
20.1 -0.9
19.5 -0.5
18.0
17.5
17.0
16.5
16.0
15.5
14.5
13.5
12.5
⟨11⟩ ⟨10⟩ ⟨11⟩ ⟨10⟩ ⟨11⟩
AZIMUTHAL ANGLE Φ
0° 45° 90° 135° 180°

Fig. 3