Spectrometer for momentum-resolved bremsstrahlung spectroscopy

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A spectrometer for momentum-resolved and polarization-dependent bremsstrahlung spectroscopy (inverse photoemission) in the vacuum UV range is described and the performance of the apparatus is discussed. A Seya-Namioka monochromator combined with a position-sensitive channel plate device for parallel detection of a wavelength range of 165 Å is used as a photon detector and covers an energy regime from 10 to 40 eV with a resolution of 5 Å. Due to the polarization-dependent reflectivity of the gold-coated gratings, the monochromator is also inherently an analyzer for the polarization of the detected light. A space-charge-limited Pierce-type electron gun comprising a BaO dispenser cathode is used as an electron source with 0.1 Å⁻¹ momentum resolution. The overall energy resolution of the apparatus is 0.3 eV at 20 eV photon energy. The sensitivity is $1.8 \times 10^4$ counts per Coulomb and eV for the unoccupied $s$, $p$ bands of a polycrystalline gold sample.

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INTRODUCTION

Bremsstrahlung spectroscopy described in the terminology of solid-state or surface physics is an experiment in which the incoming particles are electrons and the detected outgoing particles are photons, which come from transitions from the free-electron-like incoming electron state into unoccupied states above the Fermi level of the investigated sample. This process is exactly the time reversal of photoemission and is described by the same type of dipole matrix element as photoemission. The new technique of bremsstrahlung spectroscopy or inverse photoemission in the UV, however, allows one to measure the energies, momenta, and symmetries of unoccupied electron states, and complements photoemission which probes mainly occupied states (unoccupied states are seen in photoemission only above the vacuum level). Inverse photoemission is analogous to photoemission in probing one-electron states while other techniques such as optical spectroscopy, electron energy loss spectroscopy, appearance potential spectroscopy, and partial yield photoelectron spectroscopy always create a hole when promoting an electron to an unoccupied state. The electron-hole interaction can be a large perturbation of up to several eV to the one-electron energies.

In a bremsstrahlung experiment, the electrons are usually emitted from a thermal cathode and the sample acts as anode. The energy of the electrons hitting the sample is given relative to the Fermi level by the potential difference between cathode and anode plus the work function of the cathode and the thermal energy of the emitted electrons. The energy of the final state into which the transition takes place is determined by subtracting the energy of the emitted photon from the initial state energy. Since the parallel component (relative to the sample surface) of the wave vector of the incoming electron is unchanged (up to a reciprocal lattice vector of the surface) by going through the surface barrier and the momentum carried by an UV photon is small compared to the electron momenta, the parallel component of the wave vector of the final state is also known. The polarization of the emitted photon finally carries information about the symmetry of the states involved.

Bremsstrahlung spectroscopy in the UV has started relatively late because the process is rather inefficient ($\sim 10^{-8}$ photons per electron into a 1-eV energy interval and 2 $\pi$ solid angle). The first experiment in the UV range was done in 1977 by Dose.¹ He used a Geiger–Müller counter to detect photons of fixed energy (9.7 ± 0.3 eV) as a function of the energy of the electrons impinging onto the sample.² This type of experiment is called bremsstrahlung isochromat spectroscopy since photons of constant energy (i.e., “color”) are detected. This corresponds to photoemission using a monochromatic light source, e.g., a resonance lamp. Isochromat spectra of various materials³ have been successfully interpreted in terms of the density of unoccupied states, especially when energy losses of the incident electrons due to electron-hole pair production are taken into account.³ Recent developments are the better definition of the angular distribution of the incoming electrons. The resulting spectra can be understood assuming direct momentum conserving transitions between Bloch states of the single-crystal samples.⁴,⁵ Recently, we have applied bremsstrahlung spectroscopy to probe absorbate states⁶ and to map out energy band dispersions.⁷ Independent from experimental progress, a theory of inverse photoemission was developed by Pendry.⁸,⁹ He showed that inverse photoemission spectra can be

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described by the same theoretical model used for the interpretation of photoemission experiments, apart from some geometrical and phase space factors.

I. GENERAL FEATURES OF THE BREMSSTRAHLUNGSPECTROMETER

The promising possibilities of inverse photoemission can be fully exploited only if the energy resolution is improved from \( \sim 0.7 \) eV for the Geiger–Müller counter systems to a value comparable with the intrinsic width of unoccupied states which is often as low as 0.2 eV. Also, a tunable photon energy is very desirable (like in photoemission) to determine cross-section variations, to tune the probing depth, and to discriminate against fluorescence photons. This can only be achieved by using a grating monochromator. The setup is shown in Fig. 1. We use a 1-m Seya–Namioka monochromator with two interchangeable gratings with groove densities of 600 and 1200 lines/mm, respectively. The two gratings cover a photon energy range from 10 to 40 eV with a resolution of 5 Å for the 1200 lines/mm grating. The reflectivity of gold-coated gratings in the Seya–Namioka geometry is polarization dependent and enhances the s component of the light by a factor of 3 compared to the p component. A position-sensitive detector allows parallel registration of different wavelengths and accepts a wavelength window of 165 Å (1200 lines/mm grating) This means we keep the energy of the initial state of the electrons constant which corresponds to constant final state spectroscopy in regular photoemission. Different final states correspond to different photon energies and are sampled simultaneously. To enhance the sensitivity of the detector assembly CsI can be evaporated in situ on the front of the first microchannel plate of the detector. A second vacuum chamber houses the electron source and can be separated from the monochromator and detector vacuum system by a metal-sealed straight-through valve. The electrons are emitted from an indirectly heated BaO dispenser cathode with a diameter of 3 mm. Two cone-shaped electrodes assure a parallel, cylindrical, spacecharge-limited electron flow in this Pierce gun. The light coming off the sample under an angle of 45° relative to the electron beam reaches the grating through a \( 3 \times 0.7 \) mm slit in the cathode electrode cone. The sample can be rotated through an axis normal to the plane of drawing of Fig. 1 in order to vary the angle of incidence of the electrons relative to the sample normal. In this geometry (further referred to as s geometry) photons with polarization parallel to the sample surface are detected preferentially, since the monochromator has higher reflectivity for s-polarized light. In order to detect the light with a polarization component normal to the sample surface we use a different geometry (p geometry). The electron beam is impinging normal to the plane of drawing of Fig. 1 onto the sample which can be rotated through an axis normal to the electron beam and to the light path. The angle between incident electrons and detected photons is 90°. The entrance slit of the monochromator is attached to the anode electrode of the electron source. For an angle of incidence of the electrons relative to the sample normal of 15° the ratio of the electric field components normal and parallel to the surface differs by a factor of 12 in going from one geometry to the other (see Sect. IV). The sample can be transferred to the separate preparation chamber through a gate valve. This avoids contamination of the BaO cathode during Ar⁺ ion bombardment or adsorption of gases onto the sample. The sample preparation chamber provides Ar⁺ ion gun, LEED optics, sample cleavage tool, and gas inlet to prepare and characterize single crystal surfaces by standard techniques. Work function changes are measured via the current/voltage characteristic of the electron gun. The samples can be heated directly through ohmic heating or by electron bombardment from a tungsten filament. Gold can be evaporated in situ onto samples in order to obtain a precise reference for the Fermi energy. The base pressure of all three vacuum chambers is in the 10⁻¹¹-Torr range. A special interlock system for the sample holders allows the changing of samples without breaking the vacuum.

The described bremsstrahlung spectrometer provides a total energy resolution of 0.3 eV (at 20 eV photon energy) and photon energies from 10–40 eV can be analyzed. Good angular definition (\( \leq 6° \)) for the electron beam and the possibility to detect the polarization of the light make this apparatus a versatile tool for measuring the unoccupied states of solids and solid surfaces. The paper is outlined as follows: after discussion of the monochromator and detector in Sec. II, the electron source is described in Sec. III. Finally, Sec. IV illustrates the performance of the combined system.

II. MONOCHROMATOR AND DETECTOR

The monochromator is a modified McPherson 1-m Seya–Namioka monochromator with the possibility...
to change between two gratings without breaking the vacuum. The gratings are replicas with groove densities of 600 and 1200 lines/mm with a blazing angle of 1° and a ruled area of 25 × 20 mm². This translates to an acceptance of f/45. The coatings (Al + MgF₂ and Au, respectively) of the two gratings provide optimum efficiency at ~10 and 20 eV, respectively. The wavelength resolution of the 1200 lines/mm grating for an 1 × 3-mm² entrance slit is 5 Å, which corresponds to 0.16 eV at 20 eV. This can be checked by observing the image of the entrance slit in direct reflection (0th order). The image of the slit is 1 mm wide and 16 mm high in perfect agreement with the expected values for this geometry. The sine drive of the monochromator permits wavelength settings with an accuracy of ±0.5 Å (1200 lines/mm grating) and is reproducible within this limit as checked by observing the 0th order for different settings at a monochromator reading of 0 Å. The wavelength calibration was checked by measuring the high energy cutoff (Fermi edge) of the bremsstrahlung spectrum for several values of the sample (anode) voltage and the corresponding wavelength settings of the monochromator. The Fermi edge was always found at the expected position within the above given limits of accuracy. The reflection coefficient of the gold coating is ~10% for light with polarization parallel to the plane of incidence (p polarization) and ~20% for light with polarization perpendicular to the plane of incidence (s polarization) for an angle of incidence of 35° 15' (Seya-Namioka mount) in the considered wavelength range. The ratio of the reflection coefficients for s- and p-polarized light for gratings similar to those we use, however, has been measured to be 314 rather than 2 for a regular gold surface. Thus, the monochromator makes it possible to measure the polarization of the photons and, therefore, to identify the symmetry of the sampled states.

The photon detector is a position-sensitive device which consists of two microchannel plates (1-in. diameter) for amplification and a resistive anode. An electronic unit calculates the position where the primary particle has hit the first channel plate, from the charge pulses at the four corners of the resistive anode. This position information is presented in the form of analog voltage levels at the X and Y outputs together with a strobe pulse (TTL) which signals the registration of a particle. The spatial resolution is specified as 100 line pairs per inch and the linearity is 5% over the entire area. From a temporarily developing ‘hot spot’ on the channel plate, which can be considered as a point source, the resolution was measured to be 90 line pairs per inch corresponding to 0.28-mm spatial resolution. To obtain a low dark rate of the detector, it is necessary to have very good vacuum conditions (<10⁻¹⁰ Torr) and to avoid any source of ions or photons in the monochromator chamber. With these precautions, we achieved a dark rate of 1.5 counts/s over the whole channel plate area, which we found to increase already at pressures in the 10⁻⁴-Torr range, whereas Wiza reports an increase of the dark rate at pressures above 10⁻⁴ Torr.

The detector is mounted tangentially to the Rowland circle of the monochromator in order to get good focusing over the entire area. This gives a practically linear wavelength scale over the horizontal coordinate (X direction) of the channel plates. Since the image of the entrance slit does not cover the whole height of the channel plate, we mask out a 15-mm high strip using the slit-width control of the electronics unit. The X output voltage of the electronic unit is measured with a pulse-height analyzer whenever a photon is detected (signaled by the strobe pulse), and the corresponding channel is incremented by one. Since the vertical direction contains no information about the wavelength the Y output is neglected. The accumulated spectra can be plotted on a X-Y recorder and read into an IBM 370 computer via a serial data line for further data processing.

The spectra accumulated in the pulse-height analyzer have to be normalized to the spatial efficiency curve of the channel plates and the efficiency of the detector, which includes reflectivity of the gratings and spectral response of the channel plates. Finally, the spectra are transformed from the wavelength scale to energies. The efficiency curve of the channel plates is measured by sweeping the 0th order with constant velocity across the channel plates, so that every point is illuminated with the same amount of photons. The efficiency of the channel plates shows variations of 20% over the usable range in the X direction (shadowing and reflection from the channel plate mounting reduces the usable width from 25 to 22 mm). The efficiency of the detector is defined as the response to “white light” shining in. We use the bremsstrahlung continuum of the sample as an approximation for a flat spectral intensity distribution. By using different samples (Ni, Au) and different electron energies, we rule out fluorescence effects or characteristic lines, band structure or density-of-states effects, and influence from diffraction in higher orders. The energy range from 15 to 40 eV (7 to 22 eV) for the 1200 (600) lines/mm grating was measured in overlapping sections, since the detector accepts only a limited wavelength window of 165 Å (330 Å, respectively). The spectra were divided by the spatial sensitivity curve of the channel plates and concatenated to form one spectrum. The good agreement of the spectra in the overlapping regions is a check for this procedure. The dashed line in Fig. 2 shows the efficiency of the detector for the 1200 lines/mm grating.

To enhance the efficiency of the detector, we evaporated in situ CsI onto the front surface of the channel plate array. CsI is known to have a very high quantum efficiency in the considered energy range and the lowest threshold of all alkali halides. The CsI single crystal was heated by a tungsten filament. A shutter prevented undesired evaporation onto the channel plates during initial outgassing of the evaporator. The evaporation was monitored with a quartz monitor. We evaporated CsI in steps of 30–40 Å and checked the detector efficiency after each evaporation. After a 600-Å-thick CsI layer had been evaporated, no further increase in the efficiency was seen and the evaporation procedure was stopped. The saturation at 600-Å thickness is in agreement with measurements.
In our experiment the whole area of the grating is used. The insert in Fig. 2 shows the quantum yield of CsI compared to the efficiency of the CsI-covered channel plates derived from the grating efficiency (dots) and the detector efficiency (line) in the lower part of Fig. 2. The channel plate response shows the same spectral features as the quantum yield of CsI, especially the minimum at 14 eV.

III. ELECTRON SOURCE

The electron gun for a momentum-resolved bremsstrahlung experiment must have good energy and angular resolution and should be capable to deliver high currents because of the low cross section for the production of photons, and the small acceptance angle of the detector. The best energy resolution could be obtained using an electron monochromator or a field emission tip, but they are not able to provide the needed electron currents of the order of 100 µA at an energy of 10 to 20 eV. This leads us to a thermionic electron emitter with a low work function such as a BaO dispenser cathode. The desired energies and currents put us into the regime of space-charge-limited electron flow even at short electron paths of the order of millimeters. The problem of using only a finite section of the space-charge-limited electron flow between two infinite extended planes—for which an exact solution is known—has been solved by Pierce by prescribing the shape of electrodes which create the appropriate fields at the electron beam boundary.

Our Pierce gun is designed as follows: the employed cathode has a circular emitting area of 3-mm diameter which also determines the diameter of the electron beam. The anode–cathode distance is 3 mm. Child’s law for space-charge-limited electron flow gives a current of 100 µA at 15 V, which is verified experimentally. The electrodes (potential 0 and 0.158φ0 in Fig. 6 of Ref. 17) have been approximated by cones with 18-mm diameter and slopes relative to the cathode surface normal of 65° and 86°, respectively. The cones are made from circular discs of 0.08-mm tantalum sheet. The cathode electrode has a 3 × 0.7-mm2 slit covered with a Ni mesh (0.25-mm mesh spacing) which allows light from a 3 × 1-mm2 area of the sample emerging under 45° (relative to the sample surface for normal incidence) to reach the monochromator in the s geometry. For the p geometry a 4.5 × 1-mm2 slit is spot welded normal to the anode electrode and the anode aperture is covered with Ni mesh. Additional shielding makes sure that only light from the sample can reach the grating. Three Ni mesh-covered holes of 7-mm diameter in the anode electrode ensure good pumping of the electron gun. The cathode is mounted as near as possible to the cathode electrode and insulated from it to allow compensation of the contact potential difference. Most of the thermal radiation of the cathode hits the water-cooled gun support made out of copper. This minimizes heating of the electrodes so a good vacuum can be maintained near the sample surface. The heating power for the cathode filament is 3.2 W at a cath-
ode temperature of 880 °C measured with an optical pyrometer. A rough estimate gives ≤200 mW for the radiation power hitting the sample, compared to ~2 mW due to the incident electrons.

Evaporation of BaO onto the sample was reduced to below the detection level by activation of the cathode by heating for 10 s up to ~1200 °C. Before this activation procedure, contamination could be detected by observing fluorescence from the 5s and 5p levels of barium following the ionization by the incident electrons. BaO evaporated during the activation process could be seen macroscopically on the electrodes afterwards. After exposure to air we removed the BaO from the electrodes because these insulating layers charged. The work function of the cathode electrode—which can be measured since it is insulated from the cathode—stayed constant after the removal of the BaO from the first activation, indicating no significant evaporation of BaO from the cathode over ~500-h operating time. These findings are in agreement with observations of Rittner on BaO cathodes and of Lang and Baer, which used the same type of cathode for bremsstrahlung spectroscopy in the x-ray range.

The use of a space-charge-limited electron gun has the advantage that the geometry determines the relation between current and voltage. This means we need no stabilization of the emission current. Since not all electrons emitted by the cathode can reach the anode in the space-charge limit, a potential minimum is built up in front of the cathode which returns the electrons emitted with low kinetic energy to the cathode. The depth of the potential minimum increases with the cathode temperature. In order to achieve a stable shallow potential minimum, we have to keep the cathode temperature constant and as low as possible above the emission threshold. This is achieved by constant current heating of the heater filament and by cooling the gun support with water, so that warm-up effects are reduced. The potential minimum increases the mean energy of the electrons which reach the anode or sample. We observed a 0.25-eV shift to higher photon energies of the bremsstrahlung spectrum by increasing the cathode temperature from normally 880 °C to 930 °C, whereas theory would predict 0.2 eV. This slight discrepancy is within the error limits of the determination of the shift of the bremsstrahlung spectrum and of the measurement of the cathode temperature. The potential minimum is also slightly dependent on the anode voltage U since the current varies as $U^{3/2}$. This variation would be on the order of $kT = 0.1$ eV for 880 °C when going from 15 to 30 V electron energy and has been neglected since it is within the reproducibility of the wavelength calibration of the monochromator at high energies. The energy distribution of the electron current at the anode is Maxwellian with a mean energy of 2 $kT$ and a half-width of 2.5 $kT$. This gives for a cathode temperature of 880 °C an energy spread of the electron distribution of 0.25 eV. As will be shown in Sec. IV, no additional broadening of the electron energy distribution due to interaction between individual electrons in the beam (Boersch effect) is observed. This is not unexpected since in our setup current density (1.5 mA/cm²) and beam length (5 mm) are small compared to situations where the Boersch effect has been observed.

The angular spread of the electron beam is determined by several influences: (1) The thermal velocity distribution of the electrons normal to the beam with a mean energy of $\frac{1}{2}kT$ causes a widening of the beam and smearing out of the beam edges. (2) The hole in the anode distorts the field in the beam region and acts like a thin lens electron (anode lens effect). (3) Magnetic fields, approximation, and imperfections of the gun geometry and inhomogeneous emission of the cathode may also lead to distortions of the beam. These latter effects are difficult to take into account and are assumed to be smaller than the other two influences on the angular distribution. The anode lens effect is, of course, absent in our p geometry since the anode hole is covered with a mesh. For the open hole, we get a slope of the electron beam edge of 9° relative to the beam axis (Ref. 36). This overestimates the effect since the sample is very close to the anode hole in the s geometry and for normal incidence the sample covers the hole, so the effect is absent. The mean thermal energy of the electrons normal to the beam is $\frac{1}{2}kT$. For a cathode temperature of 880 °C, this translates to a momentum resolution $\Delta k = 0.1$ Å⁻¹, which is in agreement with experiment as shown in Sec. IV. The thermal velocity distribution of the emitted electrons normal to the beam causes also that some electrons hit the anode rather than passing through the anode hole as predicted by the Pierce theory. This problem has been treated in Ref. 35 and gives for our setup at a kinetic energy of 15 eV that 85% of the electron current passes through the anode hole. We find experimentally that 80% of the total current reaches the sample; the difference may be due to magnetic stray fields or imperfections in the gun geometry. As will be detailed further in the following Sect. IV, this type of a space-charge-limited Pierce gun with a BaO cathode is well suited for bremsstrahlung spectroscopy providing good energy (0.25 eV) and angular resolution (0.1 Å⁻¹) at high currents of 100 μA.

IV. PERFORMANCE OF THE APPARATUS

The parallel detection capability of the photon detector leads to the following operation mode of the bremsstrahlung spectrometer. We keep the energy of the electrons constant and measure the high energy end of the photon spectrum, the cutoff corresponding to transitions into states at the Fermi level. This corresponds to constant final state spectroscopy in photoemission. This mode of bremsstrahlung spectroscopy has the advantage of keeping the initial state constant and observing the transitions between this state and the various final states above the Fermi level. Since one state is fixed, the interpretation of the spectra is much easier than in bremsstrahlung isochromat spectroscopy, where photons of fixed energy are detected and, therefore, both initial and final state are varied.

Figure 3 shows the bremsstrahlung spectrum of an evaporated polycrystalline gold film (circles). The spectrum is plotted in energies relative to the Fermi level $E_F$.
corresponding to the high-energy cutoff of the spectrum and data points above $E_F$ corresponding to lower photon energies, since the electron energy is constant (20.6 eV). The spectrum is essentially flat as expected for gold with a constant density of states above $E_F$ due to unoccupied $s$, $p$ states. Measuring a polycrystalline sample ensures an averaging of all crystal orientations, so that the spectrum reflects the density of states and is not determined by angular or initial state effects. In a 1-eV-wide section of the spectrum we have $1.8 \times 10^6$ counts per Coulomb of incident electrons. Using the $f/45$ acceptance, a 15% reflectivity of the grating\(^2\) (average for both polarizations) and 80% quantum efficiency of CsI,\(^2\) we estimate that $3 \times 10^{-10}$ photons per incident electron are emitted into the half-space. Pendry's estimate for a $d$ band\(^1\) gives $5 \times 10^{-8}$ photons per electron in half-space. The difference can be attributed to the lower emission of $s$, $p$ bands compared to $d$ bands and the optimistic assumption for the detector efficiency.

The step-like gold spectrum in Fig. 3 illustrates the energy resolution of the system. The line in Fig. 3 is the expected spectrum for a step function using the measured resolution of the detector (via 0th order) and a half-Maxwellian energy distribution for the electrons emitted at a cathode temperature of 880 °C. The photon energy resolution of 0.16 eV and the 0.25-eV FWHM of the electron energy distribution add to a total resolution of 0.3 eV. The perfect agreement in line shape between calculated and measured spectrum in Fig. 3 has been used to calibrate the effective work function of the cathode (work function of cathode plus depth of potential minimum and mean thermal energy of emitted electron current, see Sect. III) and is determined as 2.25 ± 0.05 eV.

The angular distribution of the electron beam is illustrated in Fig. 4 by a set of spectra for angles of incidence between 5° and 60°. The data were taken on a Ni(111) surface with the electron beam of 20-eV energy lying in the ILX mirror plane ([112] direction). The 600 lines/mm grating was used in the $p$ geometry. Comparing the spectra for 41° and 48° or 54° and 60°, respectively, we estimate an angular resolution of 6° or better. This translates to $\Delta k = 0.1 \text{ Å}^{-1}$ as can be seen from the left-hand scale of Fig. 4, the spectra being plotted with an offset corresponding to the parallel component of the wave vector $k_z$. The mean free path of the electrons in the sample of $\sim 10$ Å puts a theoretical limit to the $k_z$ resolution of $\sim 0.1$ Å\(^{1,11}\) so that further improvement of the angular resolution would be useless.

All spectra of Fig. 4 show strong emission near the Fermi level arising from transitions into empty $d$ states. The peak at 2 eV in the 48° spectrum ($k_z = 1.46 \text{ Å}^{-1}$) is due to transitions from $X_1$ to $X_4$ in the Ni band structure, and shows strong dispersion as we go away from $X$ on the $\Delta$ axis (spectra 54° and 60°) in agreement with band structure calculations.\(^8\) The spectra for small values of $k_z$ (5°-15°) show a small peak around 5.5 eV which goes to lower energies as we approach normal incidence. We assign this peak to transitions from states near $L_2$ into states near $L_1$ which are calculated to be at 21.7 and 6.0 eV, respectively.\(^8\) Dipole selection rules exclude transitions from $L_3$ to be seen in the $p$ geometry.\(^9\)

The spectra in Fig. 4 have been corrected for the variation of the detected photon intensity with angle. The open circles in Fig. 5 show the measured photon intensity in the 0th order as a function of angle relative to the surface normal ($p$ geometry). The data were taken on a Ni(111) sample with 60 eV incident electron energy in

**Fig. 3.** Unoccupied states of an evaporated polycrystalline gold film. The circles show the measured spectrum; the line is the calculated spectrum for a step-like density of states using the monochromator resolution and the energy distribution of the electrons emitted from a cathode at 880 °C temperature. The experiment confirms the expected resolution of 0.3 eV.

**Fig. 4.** Spectra for different angles of incidence relative to the surface normal of a Ni(111) sample. The electron beam of 20-eV energy is coming in along the (112) direction. The spectra are plotted with an offset relative to the parallel component of the wave vector (left scale).
order to avoid initial state effects due to direct transitions. Measurements at lower energy showed the same angular dependence. The decreasing intensity above 55° is due to the finite slit height, since for large angles of incidence the electron beam illuminates an area whose projection is higher than the slit height. Assuming a constant beam diameter we get a decrease like cotan Θ, as indicated by the dashed line in Fig. 5. For small angles of incidence the photons can be reflected at the sample-vacuum interface, since the light emerges under grazing angle relative to the surface in the p geometry. The solid curve in Fig. 5 shows the transmitted intensity as a function of angle calculated with Fresnel's formula. The optical constants for Ni have been taken from Ref. 40 and the ratio of the reflectivities of the gratings for the s and p components of the light was taken as 3 (see Sect. II). The interpretation of the photon intensity variation with angle by reflection of the outgoing photons has been further confirmed by measuring the photon intensity versus angle for different photon energies, which shows variations as expected from the energy dependence of the optical constants.

Figure 6 shows Ni(111) spectra for constant $k_{||}$ and different initial state energies ranging from 16 to 24 eV. The experimental conditions are the same as for Fig. 4 and the parallel component of the wave vector was chosen to $k_{||} = 1.46 \, \text{Å}^{-1}$ in order to sample states at $M$ of the projected bulk band structure which corresponds to the LXLX line in the extended zone scheme. The transitions into empty d-band states at $E_\text{F}$ are seen as in Fig. 4; the width is increasing because of the constant wavelength resolution of the 600 lines/mm grating. The peak at 2 eV above $E_\text{F}$ shows strongest intensity at 18 eV initial state energy and is the same as discussed in connection with the 48° spectrum of Fig. 4. The spectra for 22 and 24 eV initial state energy show a weak peak between 6 and 7 eV above $E_\text{F}$, which probably derives from bands connected with the s, p band at $L_1$. Figures 4 and 6 show that there are strong angular and initial state effects in momentum-resolved bremsstrahlung spectroscopy. This enables us to directly map out energy bands of solids.

The symmetry of the final states can be determined by detecting the polarization of the emitted photons. We write the dipole matrix element$^{10,11}$ for the transition from the initial state $|i\rangle$ into the final state $|f\rangle$ in the usual form (neglecting local field effects$^{45}$):

$$\langle f | p \cdot A | i \rangle,$$

where $p$ is the momentum operator and $A$ is the vector potential. The wave function of the incoming electron far away from the surface is a plane wave. Hermanson$^{43}$ has shown that the complete initial state (LEED state) $|i\rangle$ is even with respect to all symmetry operations of the semi-infinite crystal which leaves the position of the incoming electron beam invariant. If we consider the special case of the electron coming in parallel to a mirror plane of the crystal, the initial state wave function must be even with respect to the mirror plane. We define a cartesian coordinate system with the $z$ axis normal to the surface and the mirror plane parallel to the $x$-$z$ plane and expand the matrix element:

$$A_i \langle f | p_i | i \rangle + A_i \langle f | p_\perp | i \rangle + A_{i \perp} \langle f | p_i | i \rangle.$$

Since the matrix element must be invariant under reflections and the initial state has even symmetry, we see that the $x$ and $z$ components of the electric field vector select the even part of the final state wave function, whereas the odd part of $|f\rangle$ shows up with a polarization parallel to the $y$ axis. Note that the symmetry operation does not act on the external electric field vector. The dipole selection rules for high symmetry points with more symmetry elements than a single mirror plane are given in Refs. 39 and 43 for fcc and bcc lattices, and for the hcp lattice in Ref. 44, respectively.
Applying the foregoing considerations to our experimental setup we see that the s geometry measures the A₂ polarization component of the light preferentially and, therefore, samples odd states, if the electrons come in parallel to a mirror plane of the sample. On the contrary, the p geometry is more sensitive to final states with even symmetry. In this case, we see for normal incidence mostly the A₁ component of the vector potential, because the cosine distribution of the dipole radiation field suppresses the A₂ component.

Figure 7 shows spectra for the clean and p(2 × 2) oxygen-covered Ni(111) surface. The spectra are taken near normal incidence with the electrons coming in parallel to the mirror plane. The d-band peak at E₀ is more pronounced for the s geometry than for the p geometry in agreement with the dipole selection rules for transitions into these A₁ states. Upon oxygen adsorption, a state at E₀ + 1.4 eV shows up in the s geometry, whereas in the p geometry increased emission is seen at 0.3 eV above E₀. Based on the dipole selection rules the adsorbate-induced states at E₀ + 1.4 eV must be odd with respect to the mirror plane and are derived from empty oxygen 2pₓ,ᵧ orbitals. The low energy peak seen in p geometry may come from empty oxygen 2pₓ orbitals or from empty Ni 3dₓ,ᵧ states folded back by surface umklapp processes induced by the reduced p(2 × 2) overlayer symmetry.

19. MacPherson Instrument Corp., 530 Main St., Acton, Massachusetts 01720.
33. W. Knaeber, Optik (Weinmar) 54, 211 (1979), and references therein.
37. Figures 6 and 7 of Ref. 35 were used with e = 4πkT/2EC for the planar space-charge-limited diode with anode–cathode distance d and the notation of Ref. 35. (See also Ref. 36, p. 59).