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Principles and operation of a new type of electron spectrometer - ArTOF

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Abstract

A new energy and angular electron analyzer ArTOF (Angular Resolved Time of Flight) is described. The analyzer is based on simultaneous measurement of flight times and angles in an advanced electron lens system. The new analyzer combines an increase in transmission by almost three orders of magnitude with improved resolution, in comparison to standard state-of-the-art electron spectrometers. In this report we describe some design principles and we give a review of calibration and alignment procedures necessary for the use of the ArTOF on a synchrotron radiation facility. Our program scripts to handle the large datasets are also discussed. Furthermore we give a broad description of the new research fields that benefit from the use of the ArTOF and give a short summary of the first results of angle resolved photoemission measurement with ArTOF using the single-bunch x-ray pulses from the BESSY II storage ring facility.

Keywords:

ARPES, Time of Flight, Synchrotron, Electron Spectroscopy

1. Introduction

The development of new electron spectrometers is very important for advances in several fields of materials research. The crucial question in such instrument development is to combine high resolution with high transmission and preferably also with simultaneous detection of energy, angles of emission and time. Electron spectroscopy was developed by the group of K. Siegbahn (Nobel laureate 1981)[1] and today tenths of thousands of scientific reports each year are published where the main tool has been this type of spectroscopy. During the years there has been an intense instrument development. The resolution has been improved from a few eV in the beginning to sub-meV for the best instruments today. Fig. 1 shows the time development of what has been reported as the state-of-the-art performance, i.e. "high resolution". Note that the diagram is logarithmic! The first electron spec-

trometers used magnetic fields to disperse the electrons and most of the technology came from beta-spectroscopy, where only high kinetic energies (typically several tenths of keV) are of interest. This also meant that the first experiments were performed using hard x-rays (Cr and Cu anodes) and for such energies the magnetic technology was excellent. However, with the development of the technique it was realized that in most cases the chemical information from photoelectron spectroscopy was most accurately extracted from the narrowest core photoelectron lines, which are all reached with excitation energies below 1.5 keV. Here, the use of electrostatic dispersion and focussing is superior. With the development of pulsed sources, in particular synchrotron radiation and laser sources, there has also been a development of instruments based on time-of-flight schemes. Such instruments typically have a very high transmission. However, this is achieved at the expense of energy resolution, in particular above 100 eV kinetic energy.

One important step in the development of hemispherical electrostatic analyzers was the introduc-

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Figure 1: Development of resolution in photoelectron spectroscopy. We note that the development can be characterized with two solid lines. The cross-over occurred when electron lens systems were fully understood [2].

tion of imaging detectors. This type of analyser has a focal plane and an imaging detector in this plane can increase the so called information rate by at least two orders of magnitude. This concept was introduced in the beginning of the 1970:ies [3, 4], and became standard in the middle of the 1980:ies.

The development of electron lenses to the hemispherical analyzers gave a series of advantages and the transmission of the device could be effectively controlled [5]. The sample region could be efficiently separated from the analyser, the lens could yield an optimized magnification to match the entrance slit of the analyser and the lens could even be operated in a so called imaging mode giving possibilities to yield spectro-microscopic images. The lens has one space resolving dimension, and by scanning the orthogonal direction a full 2D image can be obtained. Later on, an angular resolved mode was developed, and this made it possible to obtain angular resolved spectra with unprecedented quality and much more rapid data collection than earlier [2]. A detailed review of the development of electron spectrometers and electron lenses is given by Wannberg [6].

One of the most important factors behind the rapid development of the spectroscopy is the implementation of synchrotron radiation x-ray sources to excite the spectra. With this implementation the exciting radiation could be fully tuned in the range

from a few eV to several keV, the polarization state could be freely chosen, the brilliance of the radiation increased by more than 11 orders of magnitude during a 40 year period and this source is also, by definition, pulsed. In particular, the amazing increase of the brilliance of the radiation has been used to increase the energy resolution, improve the spatial resolution and to shorten the measurement times. The pulse lengths in the storage rings are typically in the range 30-400 ps. This opens up for experiments where the timing is essential.

A new concept was developed in 2004 by researchers at the Department of Physics in Uppsala in collaboration with VG Scienta AB. This led to the construction of the ArTOF [6, 7] spectrometer. We have further developed these ideas during the last years, and the successive steps show that such an instrument can indeed be realized and can reach ambitious design goals. The fundamental principle of the ArTOF is to use time-of-flight detection to determine the electron velocities and thus the electron kinetic energies. Earlier time-of-flight spectrometers, using a drift tube where the electrons pass with constant energy, cannot give high resolution at high kinetic energies. If retardation stages are applied, the high transmission - the great advantage of time-of-flight spectrometers - is severely deteriorated. An alternative is to make a drift tube with a very long flight time. This is the idea behind the magnetic bottle spectrometer [8, 9, 10]. However, with such a concept all information on the emission angles is destroyed.

The ArTOF concept starts from an analysis of the properties of the angular resolved mode of the electron lens of the Scienta SES-200 instrument [2]. The electron optics design of the latter instrument was made by Wannberg (see Ref. [6]). In the angular resolved mode the non-energy-dispersive direction of the detector is used for detection of the emission angles. There is also a focussing property of the lens, such that parallel electron trajectories from small spots on the sample are effectively focused to the same point on the detector. This makes the angular measurement very precise.¹

In the ArTOF spectrometer a modified six element electron lens is used, operating essentially in the same mode as in the case of the angular dispersion mode of a VG Scienta SES type instrument [2]. In the imaging mode of such a spectrometer,

¹Dr. Wannberg got the 2008 Joseph F. Keithley award from APS for this development

the sample is placed in the object plane and the entrance slit of the analyzer is placed in the image plane. In contrast, the angular resolution mode is achieved by first creating a focal plane in the lens system, where all parallel rays will be focussed to one single spot. Using a point like source, this plane therefore contains information on all emission angles. However, this pattern is very small and to use the detector efficiently, the resulting image - with a suitable magnification - is projected onto the entrance slit. It should be noted that for the hemispherical analyzer the use of an entrance slit is mandatory and only the non dispersive direction of the detector will display different angles.

In the ArTOF, the energy analysis is instead made by measuring the time-of-flight. We can then use the full acceptance cone of the electron lens and we place a time resolved 2D detector at the end of the lens where the angular pattern is projected. This allows the simultaneous measurement of two coordinates x and y (i.e. two angles) and the arrival time of the electron. If all these parameters are known with high precision, the trajectory, and the corresponding velocity distribution along it, can be calculated with high precision and the kinetic energy of the emitted electrons can be accurately determined, as also the emission angles [7].

There are many experimental difficulties to overcome with such a device. The illuminated sample spot must coincide with the object point of the lens. The instrument needs a start pulse determined with high precision, and there is a need for high quality electronics to handle the pulses. The synchrotron radiation bunches at most facilities are suitable for experiments of this kind. The demand is high precision in timing, high signal to noise ratio of the rapid electronics, and less than 100 ps x-ray pulse width. We have used the storage ring facility BESSY II for our studies, with a pulse length below 70 ps (FWHM). ArTOF spectrometers can also be used in combination with pulsed lasers. However, for higher energies the repetition rate of the laser sources is still rather low which limits the count rate.

The development of the ArTOF is presently dependent on the access to single bunch beam-time at third generation storage rings. During the first phase of the ArTOF development a pulsed electron gun giving 1 ns pulse lengths was used to make proof of principle experiments. The collaboration was then extended to HZB in Berlin where the BESSY II storage ring is very suitable as an ex-

citation source for the instrument. A first report has been published from this project, showing that the theoretical concept is possible to realize experimentally [7]. The work has also resulted in finished projects, see Refs. [11, 12, 13] .

In this paper we give a review of the continued development. In subsequent single bunch test periods we have been able to design alignment procedures making the instrument ready for general use, we report on the software development, which is a crucial aspect of this instrument and we discuss the need for very high data acquisition speed. Finally we will make an overview of new experiments that will become possible using the new types of spectrometers.

2. General description

Since the start of Photo Electron Spectroscopy (PES) in the 50:ies, resolution has improved in a dramatic way over the years, from a few eV to the sub-meV range. At the same time the transmission has been increased, although not at all to the same extent. In many applications it is also essential to perform measurements with angular resolution. In valence photoelectron spectroscopy the energy band structure can be determined by performing Angular Resolved Photoelectron Spectroscopy (ARPES) measurements. In Fig.2 we give a sketch of the principles of ARPES.

In the first experiments of this kind a small and light-weight spectrometer was mounted on a goniometer. Using such an arrangement, one could measure spectra as function of emission angle, and thus the k -dispersion of the valence electron states could be determined. However, the experiments were difficult and time-consuming. Most often only single channel detectors were used. The precision in the measurement comes partly from the mechanical properties of the goniometer and partly from the acceptance angle of the spectrometer.

An alternative way to perform ARPES is to use a so called display-type analyzer as described by Eastman et al.[14]. A solid angle of as much as 1.8 sr could be imaged on a two dimensional multi-detector. This removes the need to rotate the sample in order to scan the whole Brillouine zone. The energy analysis is in this case performed by the combination of a high-pass and a low-pass energy filter. Only one energy is detected at the time and the complete characterization is achieved by scanning the pass energy. The angular resolution in

Figure 2: Definition of angles in an ARPES experiment

this spectrometer was 2° and the energy resolution in the order of 100 meV. Various other spectrometer designs have been introduced in order to measure angular resolved spectra, as for instance the toroidal spectrometers [15, 16].

In the beginning of the 1990:ies a concept was introduced for obtaining angular resolved spectra in a range of angles, using a fixed hemispherical analyzer with an electron lens [2]. The so called angular resolved mode was introduced. Dispersion curves could be rapidly measured along one cut through the Brillouin zone of the crystal. The angular resolution improved to about one tenth of a degree. For obtaining the dispersion in all directions one still had to rotate the sample. This soon became the standard way to measure Angular Resolved Photo Electron Spectra (ARPES). As was pointed out in Ref. [2], the hemispherical analyzer using a multi-detection system has a very high information rate. In the high resolution mode the transmission, however, is limited by the narrow slits in the system.

Pulsed photon sources allow the use of electron spectrometers based on time-of-flight. The advantage is the very high transmission of such instruments. In principle it is possible to achieve an acceptance solid angle of close to 4π . This is, for instance, very useful in the case of coincidence experiments.

The high transmission can be achieved in various ways. For example, an inhomogenous magnetic field can drive the electrons into the analyzer or a strong acceleration field can be used for the same purpose. The electrons subsequently enter into a drift tube of length L , where they pass with a constant velocity v and one measures the time of flight $t - t_0$. The electron energies are directly obtained using the classical expressions. The drawback of the simple drift tubes is that the resolution is lim-

ited by the fact that the trajectories have somewhat different lengths.

In the ArTOF the simple drift tube is exchanged for an advanced electron lens. The angular resolving mode of such a lens is based on the fact that the kinetic energy of the photoelectron and its take-off angles lead to a unique position at the focal plane at the end of the lens, as described above. However, the angular resolved electrons are not projected on an entrance slit but hit surface of a delay line detector. This detector measures the arrival time of the pulses and their x and y coordinates. Thus, we record in parallel the whole 2D angular pattern instead of only one angular coordinate. The energy analysis is done by measuring the time of flight. However, we use a more advanced scheme than for standard drift tube devices.

Figure 3: Sketch of a set of calculated trajectories in the ArTOF

Since all electrostatic potentials in the lens are pre-set we can calculate all the trajectories of the electrons through the lens and we can also calculate the velocities in each point along the tracks. The tracks are typically quite complicated, as can be seen in Fig. 3.

The ratio between the transmission of an ArTOF and a hemispherical analyzer is essentially given by the area of a circle with diameter equal to the length of the entrance slit in the hemisphere, divided by the area of said slit. This approximation is valid for the angular modes of the instruments since the angular dispersion is such that the angular range is matched to the slit length in the hemispherical case and the detector diameter in the ArTOF case. Furthermore, the energy windows of the compared measurements must of course also be similar.

Very high resolution measurements of low kinetic energies (in the range of 2 eV kinetic energy), require very narrow slits in the hemispherical analyzer (typically 0.1 mm). In such an experiment, with comparable energy windows and a pulsed photon source with suitable repetition rate giving a

small photon spot on the sample, the gain in transmission is up to almost a factor of 250 in favor of the ArTOF.

For the ArTOF spectrometer good angular focusing is fundamental for the operation whilst for the case of the hemispherical analyzer one can for many applications use other modes of operation, such as the intensity mode or the spatial resolution mode. Hence, if angular information is not of interest the hemispherical analyzer is in many cases more efficient in terms of information rate [2].

From the known trajectories, it is possible to construct a transformation matrix relating the measured positions x , y on the detector and the flight time t to the take off angles θ , ϕ and the kinetic energy E_k :

$$\begin{pmatrix} E_k \\ \theta \\ \phi \end{pmatrix} = \mathbf{T} \begin{pmatrix} t \\ x \\ y \end{pmatrix}$$

The matrix $\mathbf{T}$ depends in a complex way on the geometric design of the lens elements and of the electrostatic potentials. We can illustrate part of the properties of $\mathbf{T}$ in a diagram, see Fig. 7 below. The lens is cylindrically symmetric so the energies can be obtained from the measured flight times and the distance r of the pulse from the centre of the detector $r = \sqrt{x^2 + y^2}$. For a full characterization we need a number of such matrixes, one for each operation mode of the spectrometer. The realization of this detection scheme necessitates i) very rapid computer resources, ii) a rapid time and position sensitive detector, iii) a sophisticated software and iv) a pulsed source with short duration.

There are several modes of operation suitable for different experimental conditions. The resulting optimization problem is relatively complex. In a fix mode measurement the lens voltages are set to values optimized for a selected center kinetic energy. Within a certain energy window around the selected center kinetic energy the separation and uniqueness of the trajectories can be guaranteed. Naturally a large energy window is desirable. However, since the ArTOF differs from a simple drift tube the chromatic aberrations have to be considered, which limits the usable energy window. Furthermore, as a consequence of the chromatic aberrations combined with the spherical aberrations inherent in classical electrostatic lens systems, the size of the usable energy window is reduced when increasing the angular range. Strong retardation increases the energy dispersion as a function of time-of-flight, and thereby

also the energy resolution. Unfortunately strong retardation is problematic mainly because it increases the chromatic aberrations of the angular pattern on the detector. Thus, the energy resolution, and to some extent also the angular resolution, are different for different measured volumes, described as the solid angle times the energy window.

The performance of the ArTOF instrument is given by the precision of our values for the time and the detector positions. Via the transformation matrix this goes back to the size of the sample spot, to the precision of the measurement of the x and y coordinates on the detector, to the pulse length of the exciting radiation and to the response times of the electronics.

2.1. Delay line detector

A crucial component is the time and position sensitive detector. We have chosen a so called delay line detector from the Roentdeck company. The principles for such a detector is shown in Fig. 4.

Figure 4: A principle sketch of a delay line detector. In front of the detector there is a gold mesh put at a potential to reject very low kinetic energy electrons. The analyzed electrons hit a stack of two multichannel plates creating a pulse that falls on two systems of wires, one for the x - and one for the y -direction.

The construction uses a stack of two multichannel plates (MCP) with a total amplification of about 10^9 . Behind this stack there are two sets of wires, picking up the signals in the x - and y - directions, respectively. See Fig. 4. The position at the detector is obtained by comparing the arrival times of the pulses at the two ends of each of the wires. The distinct and fast pulse from the MCP discharge event is used as a measure of the arrival time of the detected electron. Further information is available e.g. in Refs. [17, 18, 19] Since there are only two sets of electrodes it is not possible to disentangle coordinates in case of multiple hits (two or more pulses

arriving simultaneously on the detector). The dead time of the detector is 100 ns. For many electron spectroscopy applications this is not a serious restriction. When high resolution is needed one anyway has to limit the number of pulses hitting the detector to approximately the same rate as the pulse frequency from the SR-source. The reason for this is that the Coulomb interaction of the electrons (space charge) will deteriorate the resolution severely if too many electrons per synchrotron radiation pulse are emitted [20, 6, 21]. Notably, this is of a special importance in the case of very small sample spots. Multi-hits on the detector are rejected in order to avoid erroneous energy and angle determinations.

For other types of applications one can consider higher detection rates (i.e. in cases where resolution is not so critical and where some broadening from space charge can be accepted). In such cases there are other types of delay line detectors on the market, where more than two electrodes are used [19].

An interesting property of the ArTOF instrument is that, in contrast to standard TOF analyzers, the electron optics acts as an energy filter. Therefore, some difficult problems of overlapping electrons with different speeds, created by subsequent pulses can be avoided. This was discussed in detail in Ref. [7]. A small drawback of the retardation potential of the lens system is that electrons with an energy close to the retardation potential are focused to close the optical axis and may create a bright spot that in the worst case burn out the center of the MCP. Therefore we implemented a scaling of the MCP front potential that follows the setting of the rest of the lens voltages so that electrons close to retardation potential of the lens system are cut off and can not enter the MCP

The power supplies that feed voltages to all the elements in the lens must be stable with meV precision. The electronics for detection of the pulses and the computer interfaces etc must have discretization rates in the order of 25 ps.

2.2. Operation of the instrument

We start the discussion using a schematic figure of the instrument. There are many situations to describe, but for simplicity we illustrate the simple case of two electrons emitted at the same time and at the same kinetic energy, but at different angles. These electrons will follow different trajectories and

will therefore arrive at different times to the detector, see Fig. 5.

Figure 5: Snapshot of the situation in the ArTOF at a certain time after the excitation pulse has hit sample. Electrons with equal kinetic energy, but emitted in different directions will experience different flight times through the lens system.

For each emitted electron the position at the detector and the flight time will depend on the kinetic energy and angle of emission. We illustrate this in Fig. 6a by using a data-set obtained for the valence band of gold, including the Fermi edge. We note that the electrons from the Fermi edge, having the highest kinetic energy, will arrive earliest to the detector. The electrons with larger angles of emission will arrive later to the detector and therefore the Fermi edge is not seen as a straight line. We have indicated the edge with a red line.

As discussed above, the raw data is in the form of an intensity diagram (specified by colors) giving the number of events as a function of (t_0, t, X, Y) where t_0 and t are the time for the exciting pulse and the time of arrival on the MCP, respectively. X and Y are the measured coordinates for the detected pulse on the delay-line detector. In Fig. 6a we have only indicated one of spatial coordinates on the detector. For each pulse we convert the data on-line to the transformed vector (t_0, E_k, θ, ϕ) by using the matrix **T** above. In Fig. 7 we illustrate a cut of this matrix in form of a diagram. The transformed data, as well as the original data are stored on a hard disc. This typically produces data-sets up to 100 Gbytes per hour.

After transformation we can produce an intensity diagram as a function of energy and emission angle. Fig. 6b shows a cut through the transformed dataset for the gold valence band of Fig. 6a. Note that in this representation all electrons originating from the Fermi surface are found at the same kinetic energy, illustrated by a red straight line.

Figure 6: (a) A cut through a dataset obtained for the valence band of gold. The x-axis refers to flight time and the y-axis to one of the detector coordinates. The time scales are referring to ticks from the pulse electronics. (b) The dataset transformed to kinetic energy and angle of emission.

3. Commissioning remarks

3.1. Calibration of the detector response

Due to lensing effects of the voltages inside of the DLD detector there is a non-linear correlation between hit position and readout. To a large extent this can be compensated for by optimizing the potentials inside the detector. In order to measure the distortions in the detector, a mask consisting of a well-defined array of holes is mounted in front of the MCP in the detector unit. Then all detector voltages are scanned while the detector is homogeneously illuminated. The resulting dataset is processed to select the voltage combination with the smallest distortions. In the next step the mask image at the optimal setting of the detector voltage is used to create a transformation matrix which relates the input and the output correctly. This matrix is used later to get the precise position of a hit. Such a calibration does not require access to a pulsed source. Any kind of UV light source (e.g. a Hg or He lamp) can be used.

Figure 7: A diagram illustrating how the kinetic energies (marked by red solid lines) and the emission angles (marked by black solid lines) are extracted from the combination of flight times (y-axis) and detector position (x-axis).

3.2. Calibration of the timing system

All times in the measurement sequence are related to the storage ring master clock signal. For the time-of-flight measurement we first of all need to know how this clock signal relates to the time when the x-ray pulse hits the sample, t_0 . It can be determined by using photons scattered from the sample, the manipulator, the sample holder or any surface in vacuum that is placed in the sample position. By setting all elements in the ArTOF to a large negative voltage and applying high negative detector bias voltage we can get a clean photon signal at the detector (see Fig. 8). These photons will reach the detector at the time t_{phot} . We can determine the t_{phot} by fitting the measured data with a Gaussian profile.

Figure 8: A diagram showing a measurement to determine the time t_0 . See text.

Knowing the distance between the sample and the detector, L , and the speed of light, we obtain t_0 as $t_{phot} - L/c_0$. This value can be directly used in the acquisition software.

Another important value we can obtain from the photon peak fit is its width which corresponds to

the overall time resolution of the acquisition system and defines the ultimate resolution.

3.3. Resolution calibration

The energy resolution depends on the time resolution in a complex way though a transformation matrix. However, for most of the practical purposes it can be estimated by the following empirical formula:

$$\Delta E = \sqrt{(\alpha E^{\frac{3}{2}} \Delta t)^2 + (\beta \Delta d \gamma E)^2}, \quad (1)$$

where Δt is the time resolution of the acquisition system, Δd - the detector resolution and E is the selected center energy.

The parameters α , β and γ are properties of the transformation matrix. For time resolution better than 3 ns the estimated error of the formula is less than 1%. In Fig. 9 we show a fit to the Fermi level

Figure 9: The Fermi level region of the EDC for the topological insulator Bi_2Se_3 together with the fit.

cut off in Bi_2Se_3 measured at 8.1 ± 1.5 K. The derived Gaussian contribution is 3.9 ± 0.4 meV. Applying eq.(1) we obtain with the used experimental parameters a value of 3.8 meV. The latter value was calculated assuming 14 eV kinetic energy and 10% energy window.

4. Data processing

Under normal operation an ArTOF instrument produces a huge amount of data since each event is stored in a data-base as a three component vector (X,Y and T for the raw data and Energy, ϕ and θ for the converted data).

This task is handled by the ArTOF Studio Console (ASC) – standard software provided by VG Scienta. The ASC produces the data as a list of events

in a binary format. In order to process the information in the database we have used the IGOR PRO program package [22], and we have developed a set of scripts for different data-processing steps. Those scripts provide a user of the system with graphical user interfaces, allowing loading and processing of both raw and analyzed data.

Before data is loaded the scripts automatically calculate all necessary parameters and ranges from a selected dataset. The data loading step consists of creating a 3D histogram of the recorded events. The single event nature of the data files allows to perform further transformations of the data before they are binned into a 3D matrix without any practical loss of the precision. It also allows to load only the required subset of the data, to freely control the step size of the data matrix, to rotate the coordinate system and to shift its center while loading the data. In order to speed up the data loading, all transformations and binning codes are programmed in C and loaded in Igor as binary extension.

The untransformed, raw data are mostly used for processing and fitting of the photon peak. Once a data block containing only the scattered photons is loaded it can be further automatically processed providing t_0 value and time resolution information.

The analysed data can be loaded in three different coordinate systems:

1. A "spherical" system, corresponding to the original coordinate system provided by the ASC. The coordinates are in this case essentially E_k , ϕ , θ as defined in Fig. 2
2. A "bi-polar" coordinate system, which perhaps can be seen as more intuitively simple. This is a coordinate system where the two angles are orthogonal. Such a system is illustrated in the Fig. 10a.
3. a "k-space" coordinate system where the data are converted to $\mathbf{k}$ -space while loading. Such a simple system is illustrated Fig. 10b. The transformation of the angular representation to the $\mathbf{k}$ -space data is not linear, and in the case of standard hemispherical analyzers one has to interpolate in the database to go from one representation to the other. In the case of the ArTOF the transformation can conveniently be performed before binning the data, using the coordinates of the event itself and producing the desired type of binned 3 dimensional matrix.

For data inspection a 3D browser script has been

Figure 10: Coordinate systems used for presentation of data. (a) Angles two orthogonal directions and (b) k-space system

developed. It makes it possible to view different cuts in the data matrix as well as to integrate data to produce 2D or 1D sets in selected directions, e.g. in order to generate "normal" photoelectron spectra from the experimental data.

5. Experimental end station

We have operated the ArTOF spectrometers at BESSY II both for gas phase studies and for surface science experiments. We have built an end station including a preparation chamber and an analysis chamber where the ArTOF spectrometer is attached. The end station is equipped with a sample manipulator, giving possibilities both for heating the sample and for cooling it to temperatures in the range of around 10 K.

The analysis chamber is equipped with a large number of ports for auxiliary equipment, allowing for a variety of experimental set-ups. The analysis chamber is magnetically shielded using μ -metal screens. Also the preparation chamber is provided with a large number of ports and is provided with standard surface science equipment. The system is UHV compatible with a base pressure in the lower 10^{-10} mbar range.

6. Application areas

A number of research fields will benefit from the characteristics of the new type of electron spectrometers. In this section we will describe some of the areas where these properties can be used to improve the experiments and to perform new types of measurements. The parallel recording of a large range of solid angles gives a number of advantages.

One may use this to achieve more rapid measurements or to reduce the photon exposure needed to reach a certain spectral quality. In some cases the high transmission provides improved possibilities to perform very high resolution measurements. The large acceptance is particularly important for coincidence experiments since the transmission addresses the key parameter for coincidence measurements, namely the ratio between true and random coincidences. This ratio depends strongly on the transmission in the two coincidence channels.

6.1. Angle Resolved PhotoElectron Spectroscopy (ARPES)

ARPES is the most direct method to study the electronic band structure of a material. It is achieved by measuring the photoelectron kinetic energy as a function of the two components of the wave vector k_x and k_y . The component parallel to the surface of the vector $\mathbf{k}$ is conserved in the photoionization process. The ArTOF instrument allows the full detection of energy and k_x and k_y for a large range in all parameters.

In order to discuss this a bit more in detail we show a result obtained for Bi_2Se_3 [11]. In Fig. 11 we have used a 3D plotting routine to visualize the database using a subset showing the binding energy E_B and the two components of the momentum k_x and k_y . The database is very large and therefore an appropriate binning is always necessary.

Figure 11: 3-D ARPES of Bi_2Se_3

The figure shows binned data, where the color coding marks the density of events for a particular

combination of E_B and k_x and k_y . The acquisition time for this database was about 15 minutes. With our recent improvements we can now obtain this result in about 5 minutes. In most text books and scientific reports, the band structure is normally presented by a graph showing the energy of the bands versus the momentum in specific directions in $\mathbf{k}$ -space. Here the bands are illustrated in all directions, visualizing directly the symmetry. In Fig. 11 a threefold symmetry is directly visible. The Dirac cone is clearly seen, demonstrating the two dimensionality of the metallic surface of this material, with the characteristic linear dispersion of energy versus momentum.

The database illustrated in Fig. 11 can be readily cut in various directions. In Fig. 12 we show examples of such cuts in the database along different directions in $\mathbf{k}$ -space and also at different energies. The time evolution of the Bi_2Se_3 band structure will be discussed below in connection with time resolved measurements.

Figure 12: Different cuts in the database for photoemission from Bi_2Se_3 . Note that the symmetry is clearly observed in panel c), whereas panels a) and b) display cuts in different directions in the $\mathbf{k}$ -space

The database is collected while the sample is in a fixed position relative to the principal axis. In the case of the experiment in Fig. 11 we used a small spot of about $90 \mu \times 90 \mu$, which was observed during several hours of measurements [11]. This is essential since in conventional experiments one has to rotate the sample to study the band dispersion in various directions, making it difficult ensure that

one is observing the same spot on the sample.

The direct visualization of the band structure and its symmetry also provides a convenient means to orient the sample. It should also be noted that it is not particularly important to make a very exact orientation of the sample. All information necessary for the analysis is, in principle, always present in the database.

6.2. Low Dose Photoelectron Spectroscopy (LD-PES)

One of the most important properties of the ArTOF instrument is the high transmission, achieved without loss of resolution. This makes it possible to reduce the photon flux by orders of magnitude. We have been able to record high resolution ARPES data using a photon flux of only 10^{-7} photons/s. One field where this is extremely useful concerns the study of fragile systems such as organic crystals. These are often extremely sensitive to radiation damage and this is one of the most important reasons why there still exist very little data on this subject. Due to the risk for radiation damage

Figure 13: Comparison of band structure results for ARPES on a Rubrene crystal. Already after 20 minutes the band structure is obtained with approximately the same quality as in Ref.[23] After 2 hours a very high accuracy is reached.

it is necessary to perform the measurements using as low flux as possible. For a conventional measurement this may necessitate frequent changes of sample leading to difficult additions of individual spectra.

In Ref. [12] the first results on low dose photoemission applied to organic crystals have been presented. In this investigation the band structure of

Rubrene was studied. The only result obtained for a Rubrene single crystal earlier is from a report of Machida *et. al* [23] where the total acquisition time was several days. In Fig. 13 we show results using the ArTOF at BESSY II. The spectrometer was focussed on the same small sample spot during the complete measurement. The crystal was, in the standard way, made conducting by laser illumination. The synchrotron radiation flux was kept at 10^8 photons/sec. The band structure at a comparable resolution and spectral intensity with that of Ref. [23] is obtained within 20 minutes using the ArTOF. It is also seen that the much lower x-ray dose allows much longer exposure times with a corresponding improvement of the data. Furthermore, the ArTOF results are not only for the Γ -Y direction but also for all other possible directions in the Brillouine zone. It should also be noted that the fact that all individual events are stored provides a powerful means to check for possible signs of time dependent sample degradation.

6.3. Time Resolved Electron Spectroscopy

Time resolved experiments can be divided in two types: experiments where the time evolution of spectra are directly observed following some type of process in the sample and pump probe experiments.

For experiments of the first type the repetition frequency of the SR source sets the time resolution. In practice the resolution is given by the minimum number of pulses needed to give a sufficient signal in the spectrum. For BESSY II the repetition frequency is 1.25 MHz. It is possible to get an event rate approaching this number with the the detector type we use. In practice ones would need something like 1000 events for obtaining a characteristic signal, leading to an estimated limit for the time resolution for such direct observations in the order of one millisecond. An example of such a study can be found in Ref. [11]. We studied the build up of a layer of molecules on the surface of a cleaved Bi_2Se_3 crystal in vacuum. This is in turn causing a so called Rashba splitting of the bands in Bi_2Se_3 . The Bi_2Se_3 crystal was cleaved in vacuum and the measurements started immediately. The experiment was running for several hours (nothing was changed), the ArTOF only collects events, timing is achieved by binning along the time-axis of provided by the start pulses. One can very clearly observe how so called Rashba splitting of the bands evolves with time, see Fig. 14 [11].

Figure 14: Time evolution of the Rashba splitting after cleaving a Bi_2Se_3 crystal in vacuum. The figure is obtained from the same database as in Ref.[11]

Since the time of the exciting pulse is stored for each event we can always check for various degradations of the sample by extracting results from different times. This is a very valuable property of this new type of spectrometer.

In pump probe experiments we use a repetitive scheme. Here the only limitation is to get high enough repetition rate of the experiment for obtaining a reasonable spectral intensity. The time resolution will be set by the time definition of the pump and probe pulses. This implies that in the "standard operation mode", using the normal pulses from single bunch at BESSY II, the pulse length of about 40 ps gives the limit for such experiments. However, BESSY II and some other sources, are also be operated in the so called "low alpha mode" where weak pulses are circulating with a pulse length of about one picosecond. We have not yet had opportunity to explore this for pump-probe studies, but we have operated an ArTOF in this mode. Using the ArTOF the pulse is sufficient for XPS measurements on a gas target. We will explore this possibility further in the future, but we conclude that picosecond pump probe experiments using the ArTOF as probe are certainly possible.

In this context it should be mentioned that improvements are made in the so called slicing scheme to generate femto-second x-ray pulses. At the moment a few kHz can be achieved at BESSY II and the total flux is in the range of 10^8 photons/sec. This makes it interesting to explore the possibilities for pump-probe experiments using photoemission at the slicing facility.

6.4. Coincidence spectroscopy

The crucial factor for coincidence experiments is the ratio of true to random coincidences. In such

experiments it is not meaningful to just increase the intensity in general since this will mainly increase the random coincidences. The critical parameter is instead the transmission of the spectrometers. The very high transmission and energy resolution of the ArTOF is favorable for getting very high quality coincidence data with a very high ratio between true and random coincidences.

If one is using one ArTOF and one hemispherical analyzer it is not necessary to use a pulsed source. In Ref. [13] such a set-up is described, where a VG Scienta 4000 hemispherical electron spectrometer, equipped with a delay line time resolved detector, is used for the second channel. From the time of arrival of an electron together with its position at the detector and the measured kinetic energy, the flight time of the electron through the spectrometer can be calculated. It is also possible to set up coincidence experiments where ArTOF analyzers are used in both channels. In this way one can achieve optimum transmission in both channels.

Several studies have been performed on coincidences between core photoelectrons and Auger electrons (Auger Photo Electron Coincidence Spectroscopy, APECS) from several molecular core levels N_2 ($N1s$), O_2 ($O1s$), CH_4 ($C1s$) and CD_4 ($C1s$)[13]. There are several advantages of this technique over normal Auger Spectroscopy, especially if the measurements can be made with high energy resolution. One possibility is to record spectra not as function of kinetic energy in the Auger channel but as function of the sum of the kinetic energies of the photoelectrons and the Auger electrons. In this way the one gets a probe of the double hole spectra without the life-time broadening of the initial state (although the spectral profiles may be influenced by the core-hole life time through interference effects). In this way one can record Auger spectra at very high resolution also for transitions with very broad initial core-hole states, extending the applicability of the technique considerably. Another advantage of APECS is that it provides new ways to disentangle spectral features relating to different sites in the system, using the core-hole chemical shifts. Effects due to otherwise overlapping satellite transitions can also be removed.

Another interesting aspect of APECS is that it provides a way to vary the information depth also for Auger spectra. This is due to the fact that the information depth of the APECS signal depends on the mean free path for both electrons involved. In this way the information depth for the Auger sig-

nal can be tuned by varying the photon energy and thereby the escape depth of the photoelectron. This opportunity is particularly interesting for systems like liquids where there are few other possibilities to make a detailed depth profiling of the different species. For such systems there is often also of particular interest to study both single- and double-hole states.

It is also possible to use two ArTOF spectrometers for the coincidence studies. Due to the combination of high resolution and transmission this will further improve the possibilities to perform very high resolution coincidence measurements in short times. One interesting opportunity when having such a system is to look at two-electron photoemission as has for instance been discussed theoretically for correlated systems[24] and superconductors and which has also been experimentally explored [25]

6.5. Nano-PES

There are a number of factors that have to be considered when performing photoelectron spectroscopy on nano-sized samples (nano-PES). When the focal spot becomes smaller the photon density on the sample increases, which increases the risk of sample destruction. The way to reduce this problem is either to renew the sample by moving it in the beam, or to reduce the photon flux on the studied nano-sized sample spot. In the first alternative we are not looking at the same spot at the sample, making the results less accurate. In the second alternative one has to compensate the lower flux on the spot by increasing the transmission of the spectrometer in order to achieve the same statistics in the spectra. This is one of the main advantages of the ArTOF for nano-PES applications, as discussed above in connection with low-dose photoemission.

A fundamental problem for high resolution photoelectron spectroscopy from solids is also connected to the space charge effects created by the cloud of photoemitted electrons [20, 6]. This effect leads to energy shifts and to line broadenings. The magnitude of the space charge effects depends on the density of the electron charge cloud caused by all the electrons that are emitted as the sample is hit by a light pulse. The effects on the spectrum will hence depend on the number of photons in the pulse, the pulse duration and the size of the photon spot. Furthermore, the total number of emitted electrons will depend on the photon energy. In addition the effect will depend on the kinetic energy of the analyzed photoelectrons. Again the ArTOF

has the advantage that it provides an opportunity to reduce the photon flux considerably due to the much higher transmission compared to a conventional hemispherical analyzer.

The space charge effects have been investigated both experimentally and theoretically. Model calculations show that the space charge effects increase as the focal spot becomes smaller [21]. However, these effects saturate at a size of about $1\ \mu$ with no additional broadenings and shifts as the spot size is further reduced. Another important parameter is the pulse duration. It has been found that the space charge effects vary rapidly with the pulse length (τ_p) and they go approximately as $1/\tau_p$ [21]. For fs pulses this may lead to very large broadenings and shifts and it becomes extremely important to be able to reduce the photon flux as much as possible.

Another advantage of the ArTOF for nano-sized samples is that one can perform angle resolved measurements without rotating the sample. This is extremely important due to the difficulty of aligning the setup such that a nanosized object can be rotated while remaining in the focal spot of the light beam. This is for instance particularly important when studying individual grains in a larger sample. In that case it is very difficult to detect in the spectra if the focal spot is shifting as an angular scan is made. One should note that there exist a multitude of interesting samples that cannot be grown as single crystals of reasonable big size. These problems are avoided with the ArTOF and it is therefore ideally suited for e.g. nano-ARPES.

In addition, an interesting possibility that may be opened up by using the ArTOF is that one may be able to increase the pressure range for ambient pressure photoemission. The ArTOF works optimally with a circular sample spot and hence a circular window opening to a gas cell can be made very small, allowing to maintain a very high pressure gradient. However, this requires also a very small distance between the sample and the slit. This requires an extreme grazing incidence of the x-ray beam.

6.6. Further development

Application of the ArTOF to different fields of research necessitates further development the ArTOF spectrometer and its utilization. Such a program should preferably focus on the use of the instrument at future ultrabright X-ray sources.

The most urgent development concerns schemes for using hybrid mode operation of storage rings. The flight time of the electrons in the ArTOF is about 1 microsecond. Therefore the highest rate of operation of the instrument is about 1 MHz. This corresponds rather well to the single bunch frequency of many 3:rd generation storage ring facilities in Europe (BESSY II, SOLEIL, ELETTRA). However, the single bunch mode interferes severely with the activities of most user groups at SR facilities. Therefore, a scheme for filling the storage rings called "hybrid mode" is more frequently used. In such a mode one injects one large pulse, separated from the rest of the multibunch pulse train by about 100 nanoseconds. For the ArTOF in general it is of great advantage if not indispensable to use the SR light pulse as the start signal. In the hybrid mode one can introduce a mechanical chopper. If such a chopper is phase-locked to the storage ring frequency and hence synchronized to the ionizing light pulses, single-bunch extraction will be possible. We are preparing a program for incorporating such chopper devices to ensure the general applicability of the ArTOF instruments to the ultra-brilliant sources of the future. Another option is to use electronic gating of the detector in the ArTOF instrument. We will explore both possibilities.

A structured program for research concerns the improvement of time-resolved measurements and micro-second electron spectroscopy. The ultimate time resolution of the ArTOF instrument is essentially set by the flight time in the analyzer, which is around 1 microsecond. This also matches the typical repetition rate of the measurements. In order to perform time resolved measurements one can record the spectra following the repetitive perturbation created by a laser, a magnetic field, a current pulse, a sudden exposure of a gas or any other kind of perturbation. In these measurements all events are stored and good statistics can be achieved in a reasonable time. In this way the time resolution in electron spectroscopy can be increased by several orders of magnitude!

The possibility to use the ArTOF in combination with liquid micro-jets is also extremely promising. The spectrometer uses a small point like source. This matches the very small dimensions of the x-ray beam at ultra brilliant synchrotron radiation sources as well as the typical extension of the liquid micro-jet (15 micrometer). In this way the resulting quality factor may be increased by many orders of magnitude compared to what can be done

today. A development program is planned for utilizing these tantalizing possibilities. This aims at achieving more rapid acquisition, being able to handle a wider concentration range including very low concentrations of solvated ions and molecules and to be able to study systems under real conditions rather than model systems.

7. Conclusions

In this report we have given an overview of the design and operational principles for the new type of angular resolved high transmission/high resolution electron energy, time and momentum analyzer (ArTOF). We have given an account of a large number of possible applications areas, which we have identified. These range from studies of fragile molecular crystals to nano-ARPES and very sensitive pump probe electron spectroscopy studies for a wide range of time-scales down to the picosecond and femtosecond ranges. There are a number of ongoing improvements. An immediate change will allow transmission well above 12 percent with improved time characteristics. An important issue will also be to modify the concept, allowing for use at SR sources operating in hybrid filling modes.

8. References