ELECTRONIC EXCITATIONS IN SOLIDS
STUDIED USING INELASTIC X-RAY SCATTERING

Szabolcs Galambosi

Division of X-Ray Physics
Department of Physical Sciences
Faculty of Science
University of Helsinki
Helsinki, Finland

ACADEMIC DISSERTATION

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Preface

This thesis is based on research carried out at the Division of X-Ray Physics of the Department of Physical Sciences at the University of Helsinki. The inelastic x-ray scattering experiments were performed using the facilities of beamlines X21A3 at the National Synchrotron Light Source (NSLS, Brookhaven, USA) and ID16 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

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Abstract

Inelastic x-ray scattering can be used to study the electronic structure of matter. The x rays scattered from the target both induce and carry information on the electronic excitations taking place in the system. These excitations are the manifestations of the electronic structure and the physics governing the many-body system.

This work presents results of non-resonant inelastic x-ray scattering experiments on a range of materials including metallic, insulating and semiconducting compounds as well as an organic polymer. The experiments were carried out at the National Synchrotron Light Source, USA and at the European Synchrotron Radiation Facility, France. The momentum transfer dependence of the experimental valence- and core-electron excitation spectra is compared with the results of theoretical first principles computations that incorporate the electron-hole interaction. A recently developed method for analyzing the momentum transfer dependence of core-electron excitation spectra is studied in detail. This method is based on real space multiple scattering calculations and is used to extract the angular symmetry components of the local unoccupied density of final states.
List of publications

This thesis consists of an introductory part followed by five publications, which are referred to by Roman numerals I – V throughout the text.


The author of this thesis is the principal author of every publication except of III, where he is a contributing co-author. He is responsible for planning and conducting all x-ray scattering experiments and performing the data analysis for each publication. He has carried out the real space multiple scattering computations for papers IV and V. He has had an active role in the interpretation of the results and in the writing of the articles.
Contents

1 Introduction 1

2 Inelastic x-ray scattering 2
   2.1 Scattering cross section . . . . . . . . . . . . . . . . . . . . . . . . . 2
   2.2 Non-resonant inelastic x-ray scattering . . . . . . . . . . . . . . . . 3
   2.3 Valence excitations . . . . . . . . . . . . . . . . . . . . . . . . . . . 4
   2.4 Non-resonant x-ray Raman scattering . . . . . . . . . . . . . . . . . . 6
   2.5 XAS and EELS as complementary techniques . . . . . . . . . . . . . . 7

3 Description of the experiments 8
   3.1 Beamline X21A3 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 8
   3.2 Beamline ID16 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 9

4 Instrumentation and experimental considerations 11
   4.1 Basic instrumentation of IXS experiments . . . . . . . . . . . . . . . 11
      4.1.1 Source and spectrometer . . . . . . . . . . . . . . . . . . . . . . 11
      4.1.2 Spectral background and sample environments . . . . . . . . . . 13
      4.1.3 Detection of x rays . . . . . . . . . . . . . . . . . . . . . . . . . 13
   4.2 Spectrometer designs . . . . . . . . . . . . . . . . . . . . . . . . . . . 14
   4.3 Preparations for an IXS experiment . . . . . . . . . . . . . . . . . . . 15
   4.4 Data analysis . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 18

5 Summary of papers 19

6 Concluding remarks 23

References 24
1 Introduction

The electronic structure of matter may be experimentally studied using techniques based on inelastic x-ray scattering (IXS). From the historical point of view inelastic x-ray scattering dates back to the beginning of the 20th century where it played a significant role in the development of modern physics. The first IXS process discovered was Compton scattering. This type of scattering by itself was a definite proof for the particle-wave dualism of electromagnetic radiation [1]. Using Compton scattering Du Mond was able to show that the conduction electrons in metals did not follow the laws of classical physics but rather a quantum mechanical Fermi-Dirac distribution [2]. Later other resonant [3] and non-resonant [4] IXS processes were discovered and explained [5, 6]. Presently inelastic x-ray scattering techniques are actively used to study the electronic structure of a wide range of materials [7–9].

In a scattering experiment a probe such as a neutron, an electron or, like in this thesis, an x-ray photon is collided with a target and changes in the properties of the probe are observed. If the interaction between the probe and the system can be described with a sufficient accuracy, these changes may be utilized to study the properties of the target system. However, the interaction between the x rays and the electrons in a system is very weak [10]. This means that the probability that an x-ray photon scatters from an electron is small, thus a large number of photons has to be delivered at the target system in order to obtain a sufficient amount of scattering events. Presently dedicated facilities called synchrotrons are available and provide experimentalists collimated and high intensity x-ray beams.

This thesis is part of the dialogue between experimental and theoretical studies on the electronic structure of matter. The publications of this thesis report the results of modern synchrotron radiation based inelastic x-ray scattering experiments on solid state materials. The results are compared to and interpreted using theoretical calculations.

The thesis is divided into six parts. Section 2 briefly reviews the basic theoretical aspects of inelastic x-ray scattering. Section 3 describes the experimental facilities used in this work. The instrumentation requirements, spectrometer designs and data analysis of IXS experiments is discussed in Section 4. Finally, in Sections 5 and 6 the main results of this thesis are summarized.

The unit system used in this thesis is the atomic unit (a.u.) system, where \( \hbar = m_e = e = c = \alpha = 1 \) and \( \alpha \) is the fine structure constant. An atomic unit for momentum is \( 1.99 \cdot 10^{-24} \text{kgm/s} \). However, the photon energies and energy transfers are reported in electron volts (eV).
2 Inelastic x-ray scattering

In this section the theory of inelastic x-ray scattering is reviewed for the intent of understanding the IXS process from the experimental point of view. The scattering cross section is presented within the non-relativistic approximation. The valence- and core-electron excitations relevant to the scope of this thesis are considered within the framework of non-resonant x-ray scattering.

2.1 Scattering cross section

An inelastic x-ray scattering process is schematically shown in Fig. 1. A photon with an incident energy $\omega_1$, a wave vector $k_1$ and a polarization state $\epsilon_1$ is scattered by a target. The final state has a photon with an energy $\omega_2$, wave vector $k_2$ and polarization $\epsilon_2$. During the scattering process an energy of $\omega = \omega_1 - \omega_2$ and momentum of $q = k_1 - k_2$ is transferred to the target system. Through this excess energy and momentum various excitations can take place within the electron system.

In the non-relativistic limit, the interaction between the electron-system and the electromagnetic field is represented by the Hamiltonian

$$H_{\text{int}} = \sum_j \left( \frac{\alpha^2}{2} A(r_j) \cdot A(r_j) + \alpha p_j \cdot A(r_j) \right),$$

where the summation is over the electrons of the scattering system, $A$ is the vector potential of the electromagnetic field and $p_j$ is the momentum operator of the $j$th electron [10]. The cross section for a scattering process in which there is one photon both in the initial and in the final state is evaluated using perturbation theory and is given by the Kramers-Heisenberg formula [11,12]

$$\frac{d^2 \sigma}{d\Omega d\omega_2} = r_0^2 \left( \frac{\omega_2}{\omega_1} \right) \sum_{I,F} \left| \langle F | \sum_j \epsilon_1 \cdot p_j e^{i k_1 \cdot r_j} | I \rangle e^{i k_2 \cdot r_j} \right|^2 \times \delta(E_F - E_I - \omega).$$

Here $|I\rangle$, $|N\rangle$ and $|F\rangle$ stand for the initial, intermediate and the final states of the scattering-electron system having the corresponding energies of $E_I$, $E_N$ and $E_F$. The summations are taken over all these states and over all the electrons in the system, located at $r_j$. The inverse lifetime of the intermediate state is denoted by $\Gamma_N$ and $r_0$ is the classical electron radius.
The cross section consists of three terms. The first term in Eq. (2) describes the non-resonant scattering of x-rays, including both elastic (|F⟩ = |I⟩) and inelastic scattering (|F⟩ ≠ |I⟩). Resonant x-ray scattering is described by the third term. Its contribution is enhanced whenever the incident photon energy close to an absorption edge. The δ-function in Eq. (2) ensures the conservation of energy.

2.2 Non-resonant inelastic x-ray scattering

When the energy of the incident photon is far from absorption edges, the second and third terms in Eq. (2) may be neglected and the cross section simplifies to

\[
\frac{d^2\sigma}{d\Omega d\omega_2} = r_0^2 \left( \frac{\omega_2}{\omega_1} \right) (\epsilon_1 \cdot \epsilon_2)^2 \left| \langle F | \sum_j \epsilon^{i\mathbf{q}\cdot \mathbf{r}_j} | I \rangle \right|^2 \delta(E_F - E_I - \omega)
\]

\[
= \left( \frac{d\sigma}{d\Omega} \right)_{\text{Th}} S(q, \omega).
\] (3)

The Thomson cross section

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{Th}} = r_0^2 \left( \frac{\omega_2}{\omega_1} \right) (\epsilon_1 \cdot \epsilon_2)^2
\] (4)

determines the strength of the coupling of the electromagnetic field to an electron and depends only on the scattering geometry through the polarization states of the incident and the scattered photons. The other term in Eq. (3) is the dynamic structure factor

\[
S(q, \omega) = \sum_{I,F} \left| \langle F | \sum_j \epsilon^{i\mathbf{q}\cdot \mathbf{r}_j} | I \rangle \right|^2 \delta(E_F - E_I - \omega)
\] (5)

containing all the information about the electron system that is accessible via the scattering process. An informative form of the dynamic structure factor was derived by van Hove [13]

\[
S(q, \omega) = \frac{1}{2\pi} \int dt \int d\mathbf{r} e^{i\mathbf{q}\cdot \mathbf{r} - \omega t} \int d\mathbf{r}' \langle \rho(\mathbf{r}', 0) \rho(\mathbf{r}' + \mathbf{r}, t) \rangle,
\] (6)
where $\rho(\mathbf{r}, t)$ is the electron density operator and the brackets denote the expectation value taken over the ground state. From this formulation it can be seen, that $S(q, \omega)$ is the Fourier transform of the density-density correlation function over space and time. Thus by studying the dynamic structure factor in $(q, \omega)$-space the dynamics and the spatial distribution of the density fluctuations in a system can be accessed. According to Eq. (6) the magnitude of the momentum transfer $q$ and the energy transfer $\omega$ determine the spatial and time scales on which the density correlations are examined [10]. When $1/q$ is considerably larger than the relevant length scale of the system (e.g. the average inter-particle distance), mainly long range density correlations, such as collective excitations, contribute to the $S(q, \omega)$. On the other hand, when larger momentum transfer values are used, the short range and more single particle-like correlations are emphasized. A schematic energy spectrum showing the various excitations that are accessible using non-resonant inelastic scattering is depicted in Fig. 2. It should, however, be noted that in addition to the typical $\omega$ values, some excitations are observable only within certain ranges of $q$. Thus not all excitations shown in the figure can be observed at some specific value of the momentum transfer.

### 2.3 Valence excitations

Valence excitations are probed when the energy transfer in the experiment is sufficient for the excitation of valence electrons. The observed x-ray scattering spectrum is typically composed of contributions from several kinds of excitations. These include, for example, single-particle-like excitations, plasmons and excitons. The contribution of each process to the scattering spectrum depends on the momentum transfer used in
In a single particle excitation process the x-ray photon transfers some energy $\omega$ and momentum $\mathbf{q}$ to a valence electron. Consequently the electron is excited into an unoccupied state. The probability of the excitation is governed by the $\mathbf{q}$-dependent transition matrix and the density of the free states. Within the band-structure picture of crystalline solids the electron states are characterized by the energy and momentum of the electron [14]. In order to excite a valence electron from an initial state having an energy $E_1$ and momentum $\mathbf{p}_1$ into a new available state $(E_2, \mathbf{p}_2)$, the x-ray photon must provide an energy $\omega = E_2 - E_1$ and momentum $\mathbf{q} = \mathbf{p}_2 - \mathbf{p}_1$ to the electron. Using the inelastic x-ray scattering technique the energy and momentum transfers can be relatively flexibly chosen. Thus, in principle, one can map the $\omega$ and $\mathbf{q}$ dependent scattering spectrum and relate it to the band-structure of the system [15,16].

The interpretation of the experimental spectrum is, however, complicated by various factors. For instance, the excited electron and the resulting hole in the valence band interact with each other and with the rest of the electrons in the system. Several computational schemes have been proposed to deal with these kind of many-body interactions [17–19]. The approximations used in these schemes are sophisticated enough to obtain a very good correspondence between the experimental and the calculated spectra in many materials. The interpretation of the experimental data thus heavily relies on the comparison with the theoretical computations.

Within the same energy regime one can also observe other excitations, often superimposed on the single-particle excitation spectrum. *Excitons* are bound states formed by the excited electron and the resulting positive hole and play an important role in the optical spectra of semiconductors and insulators [20]. A *plasmon* is a collective electron density fluctuation which can occur when the electrons in the system respond as a whole to the perturbation caused by the x-ray photon. Prime examples of this kind of excitations can be observed in the energy loss spectra of simple metals [21,22]. The study of these excitations provides a testing ground for the development of various theoretical approaches modelling the interactions in the electron system [23,24].

The valence electrons responsible for the above mentioned excitations also define the optical properties of the material. The link between $S(\mathbf{q}, \omega)$, obtained from IXS, and the macroscopic dielectric function $\varepsilon_M(\mathbf{q}, \omega)$ [25], governing the optical properties of matter, is provided by the fluctuation-dissipation theorem [26–28]

$$S(\mathbf{q}, \omega) = \frac{q^2}{4\pi^2 n} \text{Im} \left( \frac{1}{\varepsilon_M(\mathbf{q}, \omega)} \right),$$  \hspace{1cm} (7)

where $n$ is the electron density. Provided that the dynamic structure factor is known over a sufficiently large energy range, the full dielectric function can be obtained from Eq. (7) via the Kramers-Kronig relations [28,29].
2.4 Non-resonant x-ray Raman scattering

The other type of electronic transitions studied in this thesis are the non-resonant excitations of core electrons. These kind of excitations are typically investigated using x-ray absorption spectroscopy (XAS). In that case the energy of the incident photon is close to the binding energy of an electron. The IXS method in which the incident photon energy is far from the absorption resonances, but the energy transfer $\omega$ is close to a core electron binding energy is termed non-resonant x-ray Raman scattering (XRS). The scattering cross section for XRS is described by Eq. (3).

The shape of the x-ray Raman spectrum very closely resembles that of an x-ray absorption spectrum. In the limit of small momentum transfer the exponential in Eq. (5) may be approximated by the familiar expansion $e^{i \mathbf{q} \cdot \mathbf{r}} \sim 1 + i \mathbf{q} \cdot \mathbf{r} + \cdots$. It is evident that in this approximation the dynamic structure factor obtained by XRS is governed by the same transition matrix elements as the cross section for the x-ray absorption process within the single particle approximation [5,30]

$$
\sigma_{XAS}(\omega_1) \sim \omega_1 |\epsilon_1 \cdot \langle F|r|I \rangle|^2 \delta(\omega_1 + E_I - E_F)
$$

$$
S(q, \omega) = |q \cdot \langle F|r|I \rangle|^2 \delta(\omega + E_I - E_F).
$$

The difference between the two is that in x-ray absorption the directional dependence is dictated by the polarization vector and in XRS by the momentum transfer. This similarity of the cross sections enables one to use XRS as an alternative to x-ray absorption measurements in systems where other spectroscopic methods would not be feasible due to experimental restrictions. Consecutively, x-ray Raman scattering has been successfully applied to study near-edge structures of e.g. the oxygen K-edge in water systems [31,32], solid helium under pressure [33] and the carbon K-edge in organic molecules [34]. The dependence of the XRS spectra as a function of the direction of $\mathbf{q}$ gives information on the angular orientation of the unoccupied density of states [35]. XRS can also be used as an alternative to EXAFS (extended x-ray absorption fine structure) spectroscopy [36–38].

At larger momentum transfers the higher order terms in the expansion of the exponential in Eq. (5) are no longer negligible. This increases the intensity of spectral features originating from non-dipole transitions. Compared to absorption measurements, this is a unique feature. One can enhance the probability of higher order transitions simply by increasing the value of momentum transfer. As an example, x-ray Raman scattering at low momentum transfer values from a 1s core electron results in the transition of the electron into $p$-like final state as dictated by the dipole selection rules [39]. At larger values of $q$ the transition probability of the 1s electron into states not accessible with dipole allowed transitions ($s,d,\ldots$) increases. This kind of selective enhancement of higher order transitions can be used to obtain additional information on the electronic states [40–43].
One approach for analyzing the momentum transfer dependence of XRS spectra is to use the real space multiple scattering formalism. Due to angular averaging, the dynamic structure factor for polycrystalline samples can be expressed in a simple form \cite{44,45}

\[ S(q, \omega) = \sum_l |M_l(q, E)|^2 \rho_l(E). \]  

(9)

The transition matrix elements \( M_l(q, E) \) stand for transitions from the initial core state \(|I\rangle\) to a scattering state having and energy \( E = \omega + E_I \) and an \( l \)-type angular symmetry. The local angular momentum projected excited state density of final states (\( \ell \)DOS) is denoted by \( \rho_l(E) \). From Eq. (9) it is evident that the measurable quantity, \( S(q, \omega) \), can be regarded as a linear combination of transitions into final states having various angular symmetries. If the transition matrix elements are known and experimental \( S(q, \omega) \) at several \( q \) exists then, in principle, the \( \ell \)DOSes can be found by solving the set of linear equations (9). The transition probability of a core electron into some scattering state \cite{46} is essentially an atomic property of the scatterer and consequently the transition matrix elements can be computed with a good accuracy \cite{45}. Thus this approach opens up the possibility to extract angular momentum projected components of the final state density of states from momentum transfer dependent XRS data.

### 2.5 XAS and EELS as complementary techniques

The excitations described in this Section can also be studied using inelastic scattering of electrons, i.e. electron energy loss spectroscopy (EELS). There are some practical advantages and also some disadvantages of using EELS over IXS. In electron spectroscopy large count-rates are obtainable due to the strong Coulomb interaction between the incident electrons and the electrons in the system under study. The incident electron beam can also be focussed even down to nm sizes enabling the high resolution spatial mapping of the electronic structure \cite{47}. Furthermore, compared to IXS instruments, a higher energy resolution can be routinely achieved by EELS spectrometers. Moreover, the convenience of a laboratory based and relatively inexpensive EELS instruments in comparison to large scale research infrastructures required by IXS should not be underestimated. For a concise review of EELS spectroscopy the reader is referred to \cite{48,49} and references therein.

However, the strength of the Coulomb interaction can also lead to increasing multiple-scattering problems, thus complicating the interpretation of the experimental spectra. The shallow penetrating depth of the electron beam in comparison with x rays also poses strict requirements on the sample preparation in order to avoid experimental artifacts originating from possible surface contaminants. Finally, due to the \( 1/r \) dependence of the Coulomb interaction the probability of scattering events in \( q \)-space is proportional to \( q^{-4} \) \cite{28} which renders measurements using large momentum transfer values impractical.
3 Description of the experiments

The experiments presented in this thesis were performed on two synchrotron radiation sources. The valence excitation spectra of cubic boron nitride presented in paper I were carried out on beamline X21A3 at the National Synchrotron Light Source (NSLS) situated at the Brookhaven National Laboratory, USA. The experiments on the valence excitations of MgB$_2$ and the x-ray Raman measurements from lithium fluoride, diamond and polyfluorene as reported in papers II – V were all carried out on beamline ID16 at the European Synchrotron Radiation Facility (ESRF), France. The experimental setup of the beamlines are rather similar. Both feature insertion devices as the radiation source with the possibility to vary the energy of the incident photons. The radiation is focussed onto the sample and the energy spectrum of the scattered x-rays is analyzed using a crystal spectrometer.

3.1 Beamline X21A3

Beamline X21A3 features a high resolution inelastic x-ray scattering setup situated at the NSLS, a second generation synchrotron radiation source [43,50]. The radiation is produced by a 27-pole hybrid wiggler and the white beam is filtered by several graphite filters before the radiation enters the beamline vacuum trough a beryllium window. The incident radiation is monochromatized using a four-bounce monochromator operating in the vertical plane. The monochromator is made from two channel-cut crystals utilizing an asymmetric and a symmetric Si(220) reflection in each crystal. The crystals are positioned as mirror images of each other (see Fig. 3) and consequently the position of the exit beam stays constant. The monochromatized x-rays are focussed onto the sample using a double focussing toroidal mirror with platinum coating. The demagnification ratio is 2:1. This setup gives an incident energy resolution of 0.22 eV at 8 keV in a focus point of 0.5×0.3 mm$^2$ at the sample with a measured flux of approximately 5·10$^{10}$ photons/s [43].
3 DESCRIPTION OF THE EXPERIMENTS

The scattered x-rays are analyzed using a spherically bent (bending radius = 1m) silicon crystal utilizing the (444) reflection. In order to improve the total energy resolution only the center part of the analyzer (diameter = 36 mm) was used in the experiments reported in paper I. The masking of the analyzer crystal also improves the momentum transfer resolution which is dominated by the finite size of the crystal. The analyzed photons were registered using a Si pin-diode detector. The total energy resolution of 0.4 eV at the incident energy of 8 keV was determined from the full width at half maximum of the quasielastic peak. In order to reduce air scattering the sample was kept in a vacuum chamber during the measurements. Another vacuum chamber was positioned between the sample, the analyzer crystal and the detector to minimize the absorption of the x rays along the air paths.

The boron nitride sample was pre-oriented ex-situ using Laue diffraction. The magnitude of the momentum transfer was controlled by the scattering angle $2\theta$ and its direction with respect to the crystal structure was oriented by turning the sample. The more precise in-situ orientation of the boron nitride crystal was obtained by observing appropriate Bragg reflections using a fluorescent screen.

The energy loss spectra were recorded by keeping the analyzer crystal Bragg angle fixed at a value of 86° and by tuning the incident energy. The time and energy dependence of the incident beam intensity was monitored using an air filled ionization chamber. At each momentum transfer value several energy loss spectra were measured and checked for consistency before appropriately adding the spectra.

3.2 Beamline ID16

ID16 is a high resolution inelastic x-ray scattering beamline at the ESRF. It is mainly designed for meV-resolution scattering for the study of phonons. In addition, the beamline facilitates an eV-resolution spectrometer that was used for the measurements reported in papers II – V. The experimental setup is shown schematically in Fig. 4.
The radiation was produced by three consecutive undulators (two in the experiments of paper III) and monochromatized by a fixed exit double crystal monochromator using the Si(111) reflection. The energy resolution of the incident radiation was further increased in some of the measurements by inserting an additional Si channel-cut monochromator utilizing higher order Bragg reflections. The x rays were focussed via a rhodium coated toroidal mirror onto the sample resulting in a beam size of 0.1×0.2 mm², except for the polyfluorene experiment (paper V) where a defocussed beam of 1.5×1.5 mm² was used to reduce the power density at the sample.

The intensity of the incident beam was monitored by two detectors. A pin diode monitored the intensity of the scattered radiation from a 25µm thick Kapton foil inserted in the beam. Another detector was set to monitor the scattering from a short air path. All measurements were performed with the samples placed in a vacuum chamber or under helium atmosphere and a vacuum chamber resided between the sample, the detector and the analyzer crystal. The single crystal LiF and MgB₂ samples were oriented ex-situ using Laue diffraction. All measurements were carried out at room temperature except the polyfluorene experiment (paper V) in which the sample was kept at a temperature of 20 K using a closed-cycle He-cryostat.

In most of the experiments a spherically bent silicon crystal was used as the analyzer. The reflections Si(444) and Si(555) produced an analyzer energy of about 8 keV and 10 keV, respectively. The reflected x rays were collected by a silicon pin-diode, residing on the horizontal Rowland circle together with the sample and analyzer crystal.

The polycrystalline diamond experiment (paper IV) was carried out using a germanium analyzer crystal utilizing the (880) reflection corresponding to the reflected energy of 12.4 keV. The higher energy made it possible to choose such momentum transfer values that the carbon K-edge was well separated from the maximum of the Compton profile. In this experiment the sample, the analyzer crystal and the detector were positioned such that the Rowland circle was vertical. Within this geometry a thick sample could be used, because the horizontal source size, as seen by the analyzer...
crystal, had a negligible effect on the total energy resolution.

All experiments were carried out using inverse energy scans, i.e. the incident energy was scanned while the analyzer energy was kept fixed. Each spectrum was measured repeatedly and checked for consistency before further data processing. The total energy resolution in the experiments varied from 0.3 eV to 1.9 eV depending on the monochromator and the type of the analyzer crystal.

4 Instrumentation and experimental considerations

4.1 Basic instrumentation of IXS experiments

4.1.1 Source and spectrometer

In a typical IXS experiment the incident photons are scattered by the sample and the energy loss spectrum at some scattering angle is recorded. The experimental energy resolution should match the intrinsic energy width of the excitation under study. Considering electronic excitations, this may vary from about 0.1 eV in case of excitons to a typical linewidth of 2-3 eV for conduction electron plasmons for simple metals within the small momentum transfer limit [7,21,22].

The common denominator for all non-resonant IXS experiments is the small scattering cross section. The double differential cross section for a scattering event for an electron is of the order of $r_0^2$ as shown in Eq. (4). Moreover, inelastic scattering is diffuse in angle and the spectrum can span over a wide energy range. Thus in order to observe scattering events at a reasonable rate, high intensity radiation sources have to be used. Presently this means that IXS experiments are carried out mainly at third generation synchrotron radiation sources using beamlines equipped with insertion devices, nowadays generally undulators. The intense radiation emitted by these devices is naturally confined into a small angular region. The discrete energy spectrum of undulator radiation even further increases the available intensity as more photons are already confined into the proper energy range. A narrow band of energies is selected from the incident radiation using a crystal monochromator. The obtained energy resolution depends on the type and the number of Bragg reflections within the monochromator.

The x rays scattered by the sample have to be collected by a system having a sufficient energy and momentum transfer resolution. In order to obtain eV resolution crystal spectrometers have to be utilized. The measurement of the energy loss spectrum implies that either the energy of the incident or the detected photons must be variable. The energy of the incident photons is varied by changing the Bragg angle of the monochromator. For an undulator beamline this is usually accompanied by tuning the undulator gap so that the energy of the peak intensity from the undulator follows the energy selected by the monochromator. In the case of scanning crystal spectro-
mometer the incident photon energy may be kept constant and the energy of the detected photons is varied.

All experiments reported in this thesis were carried out using crystal spectrometers selecting a fixed energy and tuning the energy of the incident photons. The advantage of this method is that the analyzer crystal and the detector operating at a fixed energy have a constant energy resolution and efficiency. These crystal spectrometers operate in an approximate point-to-point focus geometry in which, ideally, the analyzer crystal selects photons of a single energy from the radiation scattered by a point-like sample and reflects them into a detector. Usually the spectrometers deviate from the ideal situation by employing a Johann type [51] spherically bent analyzer crystal. The effect of geometrical factors such as the Johann aberration and the finite source size seen by the analyzer can, however, be minimized by operating the spectrometers in a near-backscattering geometry [51,52]. The downside of this setup is that only a single energy is recorded at a time and in some cases it may take a considerable amount of time to collect the whole energy loss spectrum.

The energy resolutions of both the radiation source and that of the spectrometer affect the total experimental energy resolution. Ideally these two should be comparable, so that neither acts as a bottleneck for the photon flux. In some experiments, however, the energy resolution has to be improved even if considerable amount of intensity is lost. An additional channel-cut monochromator can be used if the total energy resolution is dominated by the incident beam. On the spectrometer side the active region of the analyzer can be reduced by masking the lower quality outer parts of the crystal. In this thesis additional channel-cut monochromators were utilized in papers III and IV, while partial masking of the analyzer crystal was carried out in every experiment. In some experiments the source size contribution to the energy resolution can be diminished by reducing the irradiated volume of the sample. This can be accomplished via reducing the sample size or by focussing the incident beam. The technique of aligning the largest dimension of the irradiated sample volume perpendicular to the plane of the Rowland circle was used in paper IV.

The magnitude of the momentum transfer is controlled by the scattering angle and can be calculated from \( q = \frac{1}{c} \sqrt{\omega_1^2 + \omega_2^2 - 2\omega_1\omega_2 \cos 2\theta} \), where \( 2\theta \) is the angle between the incident and the scattered radiation and the other quantities are expressed in atomic units. The momentum transfer resolution depends on the spread of scattering angles which is typically dominated by the finite size of the analyzer crystal. The \( q \) resolution can be improved by limiting the size of the analyzer crystal at the expense of the rate of detected photons. In addition to the magnitude of the momentum transfer also the orientation of \( q \) can be of interest when using textured or single crystal samples, for example. The rotation of \( q \) with respect to the sample coordinate system can be achieved by mounting the sample onto a goniometer having a sufficient number of rotational degrees of freedom.
4.1.2 Spectral background and sample environments

Due to the small scattering cross section care has to be taken to minimize the spectral background. Photons originating from unwanted processes within the sample or scattering from the sample surroundings should not reach the detector. Within the sample the relative probabilities of processes that lead to fluorescence radiation, elastic- or inelastic scattering of photons can be slightly tuned by choosing the incident energy properly. In experiments using crystalline samples, the intense Bragg reflections to the direction of the analyzer crystal can be extinguished by slightly turning the sample. Nevertheless, the spectra often contain unavoidable background due to other scattering processes. For example, Compton scattering is essentially regarded as background in x-ray Raman experiments. However, at a chosen $q$-value for an XRS experiment the Compton peak resides at a fixed energy position and cannot be removed experimentally.

Photons scattered from the surroundings of the sample can be prohibited to reach the detector with a few standard measures. By placing the sample in vacuum the scattering by air in the vicinity of the sample is eliminated. For vacuum sensitive samples helium atmosphere may be used as the total scattering cross section of He is significantly lower than that of nitrogen or oxygen [53]. The high incident energies and small samples composed of light elements mean that a significant part of the incident radiation may penetrate the sample. The transmitted beam should be stopped in such a manner that it does not produce radiation that can be picked up by the detector. An additional vacuum tank between the sample, the analyzer crystal and the detector effectively reduces the possibility for the photons scattered by the sample to reach the detector without being reflected by the analyzer. More importantly, the vacuum tank reduces the length of the air path the x rays have to traverse. The slight absorption within the thin window material of the vacuum tank, typically Kapton, is by far compensated by the reduction of the x-ray beam attenuation due to shorter air paths.

The penetrating power of hard x rays enables the use of various kinds of samples and sample environments. In addition to hard condensed matter samples, liquid [31, 32] and gaseous samples [54] can also be studied using sample cells having a suitable window material. Furthermore wide range of studies can be carried out using various temperature or pressure controlled sample environments [55–58].

4.1.3 Detection of x rays

At most synchrotron radiation sources the ring current is a function of time which means that also the incident x-ray beam intensity is time dependent. Moreover, if the IXS spectrum is recorded by scanning the energy of the incident radiation the efficiency of the beamline optics as a function of energy has to be taken into account. These facts necessitate the use of some kind of incident intensity monitoring. Typical
monitoring systems utilize gas ionization chambers, pin-diodes or solid state detectors. The ionization chamber and the pin-diode operated in current mode offer a linear response over a wide energy range [59, 60]. The output current has excellent statistical accuracy but the detectors have no energy resolution. Solid state detectors offer a good energy resolution and can be used to resolve the harmonics of the incident energy. These detectors are typically set to monitor the scattered radiation from a short air path or a thin foil. However, most solid state detectors cannot be used to detect photons at a very high rate without a significant dead-time correction. Operating the detectors at a low count rate can lead to a statistical-accuracy limited monitor signal.

As the energy dispersive element within the spectrometer is the analyzer crystal, the type of detector used is usually not critical. The energy resolution of the detector can be used, for example, to discriminate the energy harmonics of the incident beam or background due to fluorescence radiation. The detector should be able to operate also at higher count rates. This is important, as in some experiments the actual signal can be superimposed on a substantial background. This can occur in XRS experiments when the observed excitation edge is in the vicinity of the Compton peak maximum.

4.2 Spectrometer designs

Several crystal spectrometer based experimental facilities [50, 61–65] on various synchrotron radiation sources worldwide have been designed for the study of electronic excitations relevant to this thesis. Each design is a tradeoff between the energy and momentum transfer resolutions and the rate of detected photons. The total count rate can be increased by collecting the scattered photons within a larger solid angle. This can be achieved by using a larger diameter analyzer crystal or positioning the crystal closer to the sample. However, the available size of crystals is limited and bending radius of the analyzer cannot be made arbitrarily small without introducing severe elastic distortions. These problems can be overcome by constructing the analyzer from several individual crystals. Large acceptance analyzers with good energy resolution based on this idea have been constructed, for example, by Bergmann et al. [63] and Cai et al. [64]. At the same time the large solid angle over which the photons are collected means a reduction in the momentum transfer resolution. Naturally, this is not a limitation in many experiments where the momentum resolution is not crucial.

The recently designed spectrometer of Fister et al. [65] also uses multiple analyzer crystals, but instead of integrating the signals with single detector the design utilizes several detectors. The analyzer crystals are positioned along a vertical Rowland circle and the signal from each analyzer is collected by an individual detector. Thus the energy loss spectra for a set of different momentum transfer values can be collected during a single scan of the incident energy. Especially for direction independent samples like powders or liquids this means a drastically reduced data collection time in experiments
probing the $q$-dependence. The recently commissioned multielement analyzer array at ID16 uses a somewhat similar approach by collecting the signals from each analyzer crystal at different portions of a 2D pixel detector [66].

The energy resolution of bent crystals due to elastic deformations scale inversely with the bending radius [67]. Thus the energy resolution of a crystal spectrometer using a bent analyzer can be enhanced by using a Rowland circle of a large radius. For example, the spectrometer on beamline BL12XU at Spring-8 [64] features a Rowland circle having a variable radius of up to 3 m and a total energy resolution of less than 100 meV has been demonstrated [68]. The decreased energy resolution of a bent analyzer due to elastic deformations can be overcome by using diced crystals [69, 70]. The energy resolution due to the finite size of the cubes can be circumvented using a 2D-detector and performing a dispersion-correction to the recorded data at each pixel of the detector [71, 72].

Nowadays many IXS spectrometers operate in the approximate point-to-point focus configuration. Also other types of spectrometers exists. The design and construction of synchrotron radiation based IXS crystal spectrometers was pioneered by Loupias et al. [73] and Schülke et al. [61, 74]. They also considered spectrometers based on energy dispersive optics and a position sensitive detector. A more recent example of this kind of configuration is the design of Hämäläinen et al. [75]. The advantage of these spectrometers is the simultaneous collection of a predefined energy window. On the other hand, the calculation or the measurement of the efficiency of the spectrometer as a function of energy is more involved. Also the large active area of the position sensitive detector can lead to significantly increased background levels.

### 4.3 Preparations for an IXS experiment

The measurement time on synchrotron sources is limited and consequently careful and sometimes laborious preparations have to carried out prior to the experiment. These include, for example, the orientation of the sample and the determination of suitable incident photon energies and scattering angles.

In order to study the directional dependence of the scattering spectra of single crystal samples, the orientation of the sample has to be determined. This can be carried out in advance by using, for example, the Laue diffraction technique. The high intensity of the synchrotron radiation can be used for the final precise positioning of the sample at the beamline by observing a few suitably chosen Bragg reflections with the help of fluorescent screen or other detector.

The energy of the incident photons in non-resonant IXS experiments can, in principle, be flexibly chosen. However, for fixed angle crystal spectrometers the availability of analyzer crystals limits the choice of energies. For example, a silicon analyzer crystal using the $(444)$, $(555)$ or $(777)$ reflection in a backscattering geometry fixes the analyzer
energy at approximately 7.9, 9.9 or 13.8 keV, respectively. The use of a higher incident energy is advantageous from several points of view. The cross section of photoelectric absorption scales with the incident photon energy approximately as \( \omega^{-3} \). Thus at higher energies less photons get absorbed within the sample or in the window materials. This is especially favorable if the sample is easily damaged by radiation. Moreover, the relative contribution of inelastic scattering to the total cross section is enhanced at larger incident energies [76]. It is also worthwhile to note that the incident energy used in the experiment defines the maximum obtainable value of the momentum transfer. On the other hand, the use of higher incident energies has also some drawbacks. Depending on the energy optimization of the insertion devices and beamline optics the total intensity may heavily decrease as the incident energy is increased. The use of high incident energy also means that higher order Bragg reflections have to be utilized with the analyzer crystals. The total efficiency of these higher order reflections is small and may thus result in a lowered rate of registered scattering events [77,78]. However, the extension of the XRS technique to 20 keV, for example, while still retaining the 1 eV total energy resolution, would increase the applicability of this method to heavier elements and new classes of materials.

Prior to the experiment suitable values of \( q \) have to be chosen. The band structure of crystalline solids naturally dictates the momentum transfers used in experiments probing the single particle-like valence excitations. The dispersion of collective- and single particle-like excitations is typically mapped out by measuring the energy loss spectra over a suitable grid of momentum transfers. In x-ray Raman scattering the choice of \( q \) depends on the purpose of the experiment. Independent on whether low \( q \) values are used to obtain x-ray absorption equivalent spectra or high values of \( q \) to emphasize the spectral contributions of non-dipole transitions, it is important to know the relative intensities of various transition channels. The expansion of \( e^{i \mathbf{q} \cdot \mathbf{r}} \sim 1 + i \mathbf{q} \cdot \mathbf{r} \) in Eq. (5) requires that \( \mathbf{q} \cdot \mathbf{r} \ll 1 \). The orbital radius of an 1s electron is of the order of 1 atomic unit. Thus based upon the expansion of the transition operator one can argue, that dipole transitions dominate as long as \( q \ll 1 \) a.u. However, a more elaborate analytical derivation shows that, essentially due to the small overlap of the core- and continuum states [79], the contribution of non-dipole transitions grows rather slowly with increasing \( q \) [46]. This is clearly visible from the experimental spectra of papers III and IV. Even at moderate \( q \) values the changes in the shape of the spectra are subtle. In addition to analytical methods [46,79,80], the relative intensity of the angular momentum channels may be estimated using momentum transfer dependent RSMS methods. Fig. 5 shows the relative contributions of the transition of the carbon 1s electron in diamond into \( s-, p- \) or \( d- \) like final states. These were computed by integrating the angular momentum projected atomic background, \( S^0_l(q,\omega) \) [44], within the energy range of 280–320 eV for various values of momentum transfer. \( S^0_l(q,\omega) \) were calculated using an extension [44] to the FEFF program [81] with a cluster size of 86
atoms. Figures like 5 can be utilized to find the most appropriate values of $q$ for the experiment.

The position of the Compton peak also restricts the possible $q$ values. The momentum transfer values used in the experiment should be chosen, if possible, such that the energy regime of interest is not in the vicinity of the maximum of the Compton peak, which resides at an energy value of approximately $q^2/2$ (atomic units). One reason for this is the lower total background. In the data analysis the theoretically calculated Compton spectra can be used for the background removal. The central region of the Compton profile is dominated by the scattering from valence electrons, whereas the outer regime is mainly due to the scattering from core electrons. In most compounds the core electrons retain most of their atomistic character and consequently their contribution to the Compton profile can, in principle, be computed with a good accuracy. Despite the reported asymmetry of the Compton profiles originating mainly from the failure of the impulse approximation for core-electrons \([82,83]\) the computed Compton profiles in this thesis were found to reproduce the experimental spectra sufficiently well in order to be used for the background subtraction.

In the experiments the radiation produced by the wiggler and the undulators was linearly polarized within the plane of the horizontal Rowland circle. The polarization dependence of the scattering enters only through the Thomson cross section Eq. (4). In the current experiments this leads to a strong suppression of the non-resonant scattering intensity in the direction perpendicular to the incident radiation. This also limits the usable values of the momentum transfer. The limitation can be overcome by positioning the plane of the spectrometer vertically, as done in the design of Fister et al. \([65]\).

The collection of the experimental spectra in several sequential scans has some merits over a single long scan. For example, each spectrum can be corrected for possible
small energy shifts before normalizing and adding up. Moreover, in the improbable situation of the loss of the storage ring current or some other technical malfunction, some of the collected spectra can be salvaged.

### 4.4 Data analysis

The sequentially obtained experimental spectra may be added up after inspecting that the individual spectra are identical within statistics. The experimental data has to be corrected for variations in the incident flux. Additional corrections are needed to account for photoelectric absorption within the sample, in window materials and air paths. If the data was collected at substantially high count rates then the detector dead-time also has to be corrected for. Due to the finite energy range measured in IXS experiments, the absorption and dead-time corrections typically contribute only a few percents. The overall statistical accuracy of the spectra may be estimated by assuming Poisson distributed number of counts at each energy step [60].

Due to the measures taken in the experimental setup, the constant background in the spectra is typically negligible. However, the removal of background caused by other processes often has to be performed. For example, in the case of K-edge x-ray Raman measurements the Compton scattering background due to other electrons has to be subtracted. As the XRS spectra are measured only over a restricted energy range, the background is often approximated by a linear function. In this thesis the background subtraction was relevant in papers III – V. In these studies, the theoretical Compton scattering spectra for each sample was computed and scaled to the experimental data prior the subtraction. The result of this approach is depicted in Fig. 6 in which the inelastic scattering spectrum of diamond is shown over an extended energy transfer range.
range. Also shown are the theoretically computed Compton scattering spectra with and without the contribution of the carbon 1s electrons.

In the data analysis one has to estimate the total accuracy of the processed experimental results. The propagation of error has to be taken into account also upon using Eq. (9) to solve the $\ell$DOS from a set of $q$-dependent XRS spectra. Since the $S(q, \omega)$ are derived from the experimental data they contain fluctuations which are reflected in the obtained $\rho_i$. The variance of these statistical fluctuations in $\rho_i$ at each energy step can be estimated using standard error propagation [86]

$$\sigma^2(\rho_i) = (\mathbf{m}^T\mathbf{m})_{ii}^{-1}, \quad (10)$$

where $\mathbf{m}$ is the scaled transition matrix having elements $m_{ij} = |M_j(q_i)|^2/\sigma_i$ with $\sigma_i$ representing the standard deviation of the statistical fluctuations is $S(q_i)$. In (10) the matrix inversion refers to the exact- or the pseudoinverse [87] of $(\mathbf{m}^T\mathbf{m})$ depending on the number of elements in $S(q)$ and $\rho_L$.

5 Summary of papers

In this thesis five individual studies on non-resonant inelastic x-ray scattering are presented with an emphasis on their experimental realization. The purpose of this thesis is twofold. First, it is part of the constant dialogue between experiment and theory. Both accurate experiments and sophisticated theoretical schemes are needed to further progress our understanding of matter. The studies in this thesis provide high quality experimental data to which the results of theoretical computations can be compared and the precision as well as possible shortcomings of the theory may be evaluated. Second, from the experimental point of view the analysis of x-ray Raman scattering spectra is further developed. The recent $\ell$DOS decomposition scheme is evaluated for two distinct systems and the possible error sources are systematically analyzed. Moreover, this thesis demonstrates that inelastic x-ray scattering can be successfully applied to study a wide variety of materials ranging from inert hard condensed matter systems to hygroscopic materials and organic polymers.

This thesis reports studies on a variety of electronic transitions including valence-, core-, collective- and single particle-like excitations. All these diverse physical phenomena can, however, be accessed using essentially the same kind of experimental setup. The type of excitation to be taken under scrutiny is selected by the proper choice of energy and momentum transfer regimes in the experiment. The common denominator for the studies reported here is the use of the momentum transfer dependence of the excitations to gain additional information on the electronic structure.

Papers I and II report inelastic x-ray scattering studies using energy transfer values ranging from a few eVs to a few tens of eVs. These experiments probe the response
of the same weakly bound electron system that dominates the electro-optical properties of matter. These properties are described by the macroscopic dielectric function \( \varepsilon_M(q, \omega) \), which plays a fundamental role in the theoretical study of the elementary excitations in many-body systems [28]. The fluctuation-dissipation theorem (7) provides the important link between \( S(q, \omega) \) obtained from the IXS experiments and the macroscopic dielectric function. Thus IXS provides a complementary technique to optical- and UV-spectroscopies for the study of the valence electron structure.

In paper I the valence electron excitations in cubic boron nitride (cBN) are reported. The electronic and crystal structures of cBN are closely related to diamond. This wide gap semiconductor also exhibits physical properties similar to that of diamond such as extreme hardness. The electronic structure of semiconductors can be described using the band structure formalism [14]. The possibility to control both the direction and the magnitude of \( q \) makes IXS an inherently well suited technique to study valence excitations in semiconductors. In practice the simple mapping of the band structure is, however, complicated not only by the \( q \)-dependent transition matrix elements but also by the interaction between the excited electron and the hole [19]. In paper I the valence electron excitations in cBN are systematically studied as a function of the momentum transfer. The experimental IXS spectra measured at several \( q \)-values along three different crystallographic directions are compared with a first principles computational scheme [15, 19]. As shown in Fig. 7 the experimental results are well reproduced by the theoretical calculations that properly incorporate the electron-hole interaction. Moreover it is demonstrated that IXS data can, in principle, be converted to and compared with optical measurements.

In paper II the valence excitations in MgB\(_2\) are studied. Magnesium diboride is a metallic compound that becomes superconductive around \( T = 39 \text{ K} \) [89], which is
the highest known transition temperature for a conventional BCS superconductor [90]. The crystal structure consists of graphite-like boron sheets intercalated with magnesium atoms. This highly anisotropic crystal structure is reflected in the directional dependence of its electronic properties. Theoretical computations predicted a very sharp plasmon-like excitation and interpreted it as a coherent charge fluctuation between the alternating B and Mg planes [88, 91]. In paper II this highly directional excitation is, for the first time, experimentally verified and the dispersion of this mode is found to be well reproduced by the theoretical computations. The experimental data show that this excitation is well defined in the first two Brillouin zones and the dispersion in the second zone turns negative (Fig. 8). The theoretical computations were limited into the first Brillouin zone and in contrast to the prediction of Ref. [91] the excitation does not decay before the boundary of the first zone. A subsequent study showed that due to crystal local-field effects the plasmon exists also in higher Brillouin zones and exhibits a remarkable cosine-like dispersion [68].

In the remaining three papers III-V results obtained from x-ray Raman scattering experiments are described. In the small momentum transfer regime XRS can be used as a complementary technique to x-ray absorption spectroscopy for low-Z elements. The use of hard x-rays generally simplifies the sample environment and reduces problems associated with possible surface effects. The common theme in papers III, IV and V is the study of the x-ray Raman spectra as a function of the magnitude of the momentum transfer. Using increasing values of $q$ to enhance the contribution of dipole forbidden transitions in the XRS spectra the angular symmetry of the final state is accessed.

In paper III the momentum transfer dependence of the fluorine K-edge is studied. Lithium fluoride is an insulator that shows excitonic features in the valence [15, 43, 92]
and in the core electron excitation spectra both at the Li [92] and at the F K-edges [93]. The experimental IXS results are compared with a first principles computational scheme [94] and a good agreement between the theory and the experiment is found. This is demonstrated in Fig. 9 which shows the experimental and theoretical results over a restricted energy range. The observed deviation from the dipole approximation in the close vicinity of the fluorine K-edge is explained by the core exciton. Using the momentum transfer dependence of the K-edge together with theoretical computations it is found that the exciton has an \( s \)-type angular symmetry.

The analysis of momentum transfer dependent XRS spectra typically relies on the comparison with theoretical calculations. In paper IV the approach of the \( \ell \)DOS decomposition method is taken to explain the \( q \)-dependence of the carbon K-edge in diamond. A merit of this approach is that the only theoretical input needed in the data analysis are the transition matrix elements, which, being essentially atomic properties of the embedded scattering atom, can be computed with a good accuracy [44]. Moreover, the transition matrix elements can be calculated within the real space multiple scattering formalism making this analysis method also applicable to nonperiodic systems such as molecules. This \( \ell \)DOS decomposition method is applied in paper IV to the much debated diamond core exciton [95–99]. The results show that the angular symmetry of the exciton is \( p \)-like. In addition, experimental and numerical factors affecting the accuracy of this technique are systematically analyzed.

Organic compounds such as polymers consist mainly of light elements and in this respect they are inherently well suited to XRS studies. Previous reports have shown that x-ray Raman scattering in the low-\( q \) regime can be successfully used as a technique complementary to soft x-ray absorption spectroscopy and inelastic electron scattering.
for the study of small aromatic molecules [100, 101]. In paper V efforts are taken to extend the use of XRS to \( \pi \)-conjugated polymer systems. Poly-[9,9-bis(2-ethylhexyl)-fluorene-2,7-diyl] (PF2/6) and its derivates form a family of promising compounds for organic light emitting device applications [102]. Partially oriented PF2/6 samples together with real space multiple scattering calculations are used to pinpoint the localization of the pre-edge excitation at the carbon K-edge to the polymer backbone. Using the momentum transfer dependence of the XRS spectra the angular symmetry of this excited state is shown to be \( p \)-like in accord with the Hückel molecular orbital model [103].

A major factor limiting the use of x-ray scattering studies of organic systems is the radiation damage [104]. In paper V measures are taken to minimize the amount of radiation damage to the sample. Various tests during and after the XRS experiments indicate that while some decrease in the long range ordering of the polymers occurs due to irradiation, the electronic and optical properties are still dominated by the PF2/6 molecules. While the exact nature of the damage cannot be pinpointed, this study indicates, that the amount of radiation damage remains below the detection level of x-ray Raman scattering. Thus with sufficient preventive measures XRS can successfully be applied to the study of organic systems. However, additional studies are needed to exactly characterize the damage of the samples due to the irradiation.

6 Concluding remarks

The five papers in this thesis report the results of non-resonant inelastic x-ray scattering experiments on a diverse set of materials. The advent of modern synchrotron radiation sources featuring insertion devices have made IXS into a feasible tool for the study of the electronic structure of matter. Presently IXS experiments can be routinely performed on many synchrotron radiation sources around the globe.

The symbiotic relationship between the experimental results and the theoretical computations has played a significant part in this thesis. The calculations were essential for the analysis of the experimental spectra. On the other hand the comparison between the experimental and the theoretical results could be used to evaluate the precision of the theoretical schemes.

Finally, instead of stressing the complementary nature of low-\( q \) IXS to optical spectroscopies for valence excitations or to x-ray absorption in the core excitation regime, the emphasis of this thesis has been on the momentum transfer dependence of the excitation spectra. The current work demonstrates how the dependence of the scattering spectra on both the magnitude and the direction of the momentum transfer can be employed to gain additional information on the electron system. The use of \( q \)-dependence culminates in applying x-ray Raman scattering to access the angular symmetry components of the electron final state.
References


