Inelastic X-Ray Scattering at the National Synchrotron Light Source

C.-C. Kao, W.A. Caliebe, J.B. Hastings
National Synchrotron Light Source, Brookhaven National Laboratory Upton, New York 11973

K. Hämäläinen
Department of Physics, P.O. Box 9, FIN-00014 University of Helsinki, Finland

M.H. Krisch
European Synchrotron Radiation Facility, F-38043 Grenoble Cedex, France
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Abstract

The research program at the inelastic x-ray scattering beamline at the National Synchrotron Light Source is focused on the study of elementary excitations in condensed matter with total energy resolution on the order of 0.1 eV to 1.0 eV. Results from selected experiments are reported to demonstrate the capability of the beamline as well as the information can be obtained from inelastic x-ray scattering experiments.
Inelastic x-ray scattering, complementary to inelastic light scattering, electron scattering, and neutron scattering, is becoming an important experimental technique in the study of elementary excitations. The inelastic x-ray scattering program at the National Synchrotron Light Source (NSLS) is focused on the study of electronic excitations in condensed matter with total energy resolution of 0.1 eV to 1.0 eV. It is developed by an insertion device team, including the Advanced Photon Source, AT&T Bell Laboratories, Brookhaven National Laboratory, the European Synchrotron Radiation Facility, State University of New York at Stony Brook, and University of Helsinki. The radiation source is a 27-pole hybrid wiggler located at one of the straight sections of the 2.5 GeV x-ray ring. The X21 phase I beamline, which was commissioned during 1993 and became operational since 1994, consists of a focusing Rowland circle monochromator, and a high resolution backscattering spectrometer. Detailed description of the beamline and the backscattering spectrometer has been reported previously [1] [2]. It is designed to allow initial experiments to be performed with total energy resolution of 1 eV, and to provide a facility for the testing of new optics [3] [4]. In this paper the kinematics of inelastic x-ray scattering and the derivation of the scattering cross section will be reviewed. Selected examples from X21 will be used to illustrate the information can be obtained from inelastic x-ray scattering experiments.

The kinematics of an inelastic x-ray scattering experiment is illustrated in figure 1. The incident photon with energy $E_1$, wavevector $\kappa_1$, and polarization $\epsilon_1$, is scattered by the sample into energy $E_2$, wavevector $\kappa_2$, and polarization $\epsilon_2$. The energy transfer $\Delta E$ is given by $E_1 - E_2$, and the momentum transfer $\frac{4\pi}{\lambda} \sin(\theta/2)$, where $\theta$ is the scattering angle. The double differential scattering cross section for inelastic x-ray scattering is derived from the photon-electron interaction Hamiltonian, the same as that for elastic x-ray scattering [5] [6].

$$\frac{d^2\sigma}{d\Omega d\omega_2} = r_o^2 \left( \frac{\omega_2}{\omega_1} \right) \sum_{i,j} \left[ \langle f | \sum_j \exp(iq \cdot r_j) \mid i \rangle (\epsilon_1 \cdot \epsilon_2) \right]$$

$$- \frac{1}{m} \sum_n \left\{ \langle f | \epsilon_2 \cdot \sum_j p_j \exp(i\kappa_2 \cdot r_j) \mid n \rangle \langle n | \epsilon_1 \cdot \sum_j p_j \exp(i\kappa_1 \cdot r_j) \mid i \rangle \right\} \frac{E_n - E_i - \hbar \omega_1 - \frac{1}{2} i \Gamma_n}{E_n - E_i}$$
In equation (1), only matrix elements arise from the $A^2$ term in first order and the $\mathbf{A} \cdot \mathbf{P}$ term in second order are included. Terms originated from the direct interaction of magnetization densities with the radiation field, which lead to magnetic Compton scattering and non-resonant x-ray magnetic scattering [7], are neglected here because the cross sections from these terms are smaller than that for charge scattering by $(\frac{\hbar \omega}{mc^2})^2$ (\sim 2 \times 10^{-4} for 8 keV x-rays).

When the photon energy is far away from any absorption edge of the sample, the inelastic scattering cross section is dominated by the $A^2$ term. Equation (1) can be reduced to the product between the Thomson scattering cross section of a free electron and the dynamical structure factor, $S(q,\omega)$, of the sample. $S(q,\omega)$ in turn is related to the frequency- and wavevector-dependent dielectric responses of the sample through the fluctuation dissipation theorem [8]. Issues such as band structure effects, local field effects, and electron correlation effects in the dielectric response of the scattering system can be addressed in detail [6].

At the moment, these measurements are still severely limited by the incident photon flux that only low $Z$ elements and their compounds can be studied. Nevertheless, inelastic x-ray scattering is the only technique that can probe the full momentum transfer range of the dielectric response, especially at intermediate $q$ range where electron scattering suffers from the effects of multiple scattering. Furthermore, since the bulk property of the sample is measured in inelastic x-ray scattering experiments, no special preparation of the sample is needed, and conditions of the sample surface is not important. It also offers greater flexibility in sample environment than electron scattering. One example is a recent comparative study of the dynamical structure factors of solid versus liquid alkali metals by Hill et al [9]. The long standing controversy over the origin of the the lineshape of the response functions for alkali metals in the intermediate $q$ range was approached by comparing the response functions of solid Na and Li with those of liquid Na and Li. It was found that
while the overall lineshape showed little change between solid and liquid, the fine structures disappeared upon melting. These findings show that the overall lineshape is dominated by electron correlation effects, while the fine structures can be attributed to band structure effects. At X21, the study of dynamical structure factors has also been extended to 3d transition metals and their compounds [10] [11]. For example, Macrander et al. [10] measured valence electron excitations in single crystal Ti and TiC. Detailed assignments of the observed valence excitations features were given by comparing the data with the calculated dynamical structure factors. It should be noted that this is one of the few cases where direct comparison between experimental data and calculations have been made because the difficulty in performing these calculations and the scarcity of reliable experimental data.

For energy transfers in the range of core electrons binding energies, $S(q,\omega)$ can be related to core electron absorption coefficients [12] [13]. The orientation of the momentum transfer can also be used to obtain information similar to polarization dependent absorption measurements [14]. Moreover, due to the finite momentum transfer in the scattering process, contributions from higher order terms in the expansion of the transition matrix elements can be significant, i.e. dipole-forbidden transitions could be observed. An example is a study of the Li K absorption edge in LiF by Caliebe et al. [15]. Figure 2 shows a series of inelastic spectra measured with momentum transfer ranging from 1.1 Å$^{-1}$ to 7.5 Å$^{-1}$ and energy transfer close to the Li K absorption edge energy. The observed energy loss peak shifts from 62.5 eV at the smallest $q$ to 61.5 eV at the largest $q$. The data can be fitted with two peaks having different $q$ dependent peak intensities. The higher energy peak is assigned to the 1s to 2p dipole-allowed transition, while the lower energy peak is assigned to the 1s to 2s dipole-forbidden transition. These assignments are consistent with the observed stronger $q$ dependence of the intensity for the lower energy peak. Similar behavior was also observed by inelastic electron scattering, although the momentum transfer was limited to below 2.25 Å$^{-1}$ [16].

In the high momentum transfer limit, the inelastic scattering spectrum is dominated by Compton scattering from both the valence electrons and the core electrons. Within
appropriate limits, the inelastic scattering cross section can be used to determine the ground state momentum distribution of the scattering electrons [17]. The total energy resolution of 1 eV at about 8 keV achieved at X21 can be translated into momentum resolution of 0.01 atomic unit (a.u.), a value significantly better than the momentum resolution of 0.1 to 0.15 a.u. achieved by a number of high resolution Compton spectrometers recently [18] [19] [20]. Although the relatively low photon energy severely limits the selection of samples to a few low Z elements, this unprecedented momentum resolution nevertheless provides an unique opportunity to the study of Fermi surfaces related features and electron correlation effects in Compton profiles. Experiments on Be [21], Li, and Na have been performed.

In equation (1), the contribution of the A·P term to the cross section can be significantly enhanced by tuning the incident photon energy near an absorption edge of the sample to exploit the the resonant conditions of the matrix elements [22]. It is usually referred to as x-ray resonant Raman scattering (XRRS), or x-ray resonant inelastic scattering. The development of synchrotron radiation as an intense and tunable x-ray source has made it possible to study the energy dependence of XRRS in greater detail and with better energy resolution. It is also possible to test many theoretical predictions and to develop new applications of XRRS.

In fact, immediately after the first observation of XRRS, theoretical work already pointed out that the scattered spectrum is expected to contain information typically obtained from x-ray absorption measurements [23]. Within one-electron picture, ie ignoring the interaction between the excited electron and the core-hole, it was predicted that both the near edge fine structures and the extended fine structures in the x-ray absorption spectrum should be reflected in the scattered spectrum. Although several experimental observations of absorption fine structures in XRRS spectra have been reported [24] [25], high resolution data are becoming available only recently. In the following, an XRRS study of NiO will be used as an example. Figure 3 shows a series of resonant Raman spectra taken at incident photon energies near the Ni K absorption edge energy of NiO, 8334 eV. The energy range of the scattered spectra was chosen to be close to that of the Ni K\textgreek{\alpha} fluorescent line, about 8265 eV.
Five distinct features can be identified in these spectra, and are labeled from A to E. These features show clear linear dispersion with the incident energy as expected from the resonant Raman process. Furthermore, features A to E can be shown to correspond to the near edge fine structures in the Ni K absorption spectrum of NiO [26]. There are several advantages of measuring the x-ray absorption near edge fine structures using resonant Raman scattering. The lifetime width of the core hole in the absorption spectrum is replaced by the narrower lifetime width of the shallower core hole in the final state in the XRRS process. Both the incident and the scattered photon energies are below the absorption threshold, so that the saturation effect and self-absorption effect are minimized. The signal-to-background ratio should also be better.

The one-electron approximation mentioned in the previous section breaks down when the interaction between the excited electron and the core-hole cannot be neglected, and many-electron effects in the resonant Raman process need to be included. A clear illustration of the need for many-electron description is given by a series of high resolution x-ray resonant Raman scattering studies of rare earth elements and their compounds, including Gd [27], Er [28], and Ho [29]. XRRS near the L_{III} edges of these rare earth elements and their compounds were measured. The energy range of the scattered spectra were chosen to be close to that of the 3d to 2p fluorescent lines of the rare earth ions. In the scattered spectra, spectral features corresponding to 3d^94f^{s+1} and 3d^94f^m5d^1 final states were clearly separated because of the large difference in the Coulomb energy for these two final states, an indication of the importance of the interaction between the excited electron and the core hole. As a result, the 2p to 4f quadrupolar transition in the L_{III} absorption spectra, which cannot be resolved from the 2p to 5d dipolar transition in the normal x-ray absorption measurement due to large core hole lifetime, was uncovered.

A further step in the direction of resonant inelastic magnetic scattering is achieved recently by excitation of XRRS from a magnetized sample with circularly polarized x-rays [30] [31]. These studies were made possible by the progress in the development of elliptically polarized insertion devices as well as novel x-ray optical elements for the conversion
and analysis of elliptically polarized x-rays. Figure 4 shows the spin-resolved XRRS spectra from a magnetized Gd metal film [30]. In this case, a LiF phase plate was used to convert the linear polarized x-rays into circularly polarized x-rays. The incident energy was tuned to the energy corresponding to the 2p to 4f quadrupolar transition in Gd. The energy range of the scattered spectra were again chosen to be close to that of the 3d to 2p fluorescent line of Gd. The two spectra shown in the figure were measured with the magnetization of the sample and the direction of the photon spin either parallel or antiparallel, similar to the arrangement of the sample and the photon helicity in a magnetic circular dichroism (MCD) experiment. Although more theoretical work is needed, these results clearly demonstrated that the final states of the XRRS process, 3d⁹⁴P⁹⁺ and 3d⁹⁴P⁰⁵¹, are strongly spin-polarized. This type of experiment, in principle, should provide information complementary to that obtained from MCD experiment and spin-resolved photoemission experiment.

Finally, an important step in the development of x-ray magnetic scattering was the discovery of large resonant enhancement of the magnetic scattering cross sections [32] [33]. Since inelastic scattering cross section is governed by the same interaction Hamiltonian, large resonant enhancement of inelastic scattering cross sections was also anticipated. In this section, one such example, resonant enhancement of the charge transfer excitation in NiO, will be shown here [3-1]. In the experiment, inelastic x-ray scattering spectra near the NiO valence band emission energy were measured as the incident photon energy scanned through the Ni K absorption edge. Curve (a) in figure 1 shows the Ni K edge absorption spectrum of NiO. Curve (b) is the normal x-ray emission spectrum corresponding to the decay of the valence electrons of NiO into the Ni 1s core hole, usually referred to as the K⁺ fluorescence spectrum. Curve (c) is the inelastic scattering spectrum measured with the incident photon energy tuned to the peak of the absorption spectrum. A new spectral feature, in addition to the valence band emission spectrum, appears in the spectrum with energy higher than that of the absorption threshold. The new feature can be roughly fitted with two peaks. The energy separations between the two peaks and the elastic line are about 4.9 eV and 7.8 eV, respectively. The average energy transfer of this new feature is
about 6.5 eV, close to the recently reported anion-to-cation charge transfer energy of NiO [35]. Moreover, this new feature shows very large resonant enhancement. The on-resonant cross section is estimated to be on the order of 100 times the off-resonant cross section. This large enhancement is very important because high energy resolution inelastic x-ray scattering is still severely limited by the incident photon flux even with new synchrotron radiation sources. It also points out the need to develop non-backscattering high resolution optics.

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FIGURES

FIG. 1. The kinematics of an inelastic scattering experiment.

FIG. 2. $q$ dependent inelastic scattering spectra from LiF. The vertical lines indicate the two peak positions corresponding to $1s$ to $2p$ (6.25 eV) and $1s$ to $2s$ (6.15 eV) transitions.

FIG. 3. High resolution resonant Raman spectra from NiO

FIG. 4. Spin-resolved resonant Raman spectra from Gd.

FIG. 5. (a) Ni K absorption spectrum of NiO; (b) Normal valence band x-ray emission spectrum of NiO; (c) Resonant inelastic x-ray scattering spectrum of NiO obtained with the incident photon energy tuned to the main peak of the absorption spectrum (a).
Inelastic X-Ray Scattering

\[ \Delta E = E_1 - E_2 \]

\[ Q = \frac{4\pi \sin(\theta/2)}{\lambda} \]