High-resolution XES and RIXS studies with a von Hamos Bragg crystal spectrometer

J. Hoszowska\textsuperscript{a,*}, J.-Cl. Dousse\textsuperscript{b}

\textsuperscript{a} European Synchrotron Radiation Facility, 6 Jules Horowitz, F-38043 Grenoble, France
\textsuperscript{b} Department of Physics, University of Fribourg, Ch. du Musée 3, CH-1700 Fribourg, Switzerland

Available online 20 March 2004

Abstract

The high-resolution von Hamos Bragg crystal spectrometer was constructed for the study of K X-ray emission from low-Z elements and L and M X-ray spectra of medium to high-Z elements. Recently, this instrument was applied to high-resolution XES and RIXS studies using X-ray synchrotron radiation at the ID21 and BM5 beamlines at the ESRF. An outline of the spectrometer design and performance characteristics will be given. The studies deal with the energy dependent KL double photoexcitation of argon, the L\textsubscript{3} and M\textsubscript{1} atomic-level widths of elements \(54 \leq Z \leq 77\), and the evolution of the K-edge RIXS spectra of manganese oxides.

Keywords: High-resolution X-ray spectrometer; XES; RIXS; Atomic-level widths; Double photoexcitation

1. Introduction

High-resolution X-ray emission spectroscopy represents a powerful tool for the investigation of electronic properties and the study of inter-shell processes. Indeed, it continues to contribute to our understanding of atomic structures and dynamics as well as of electronic states in solids. With the advent of high-brilliance X-ray synchrotron sources there has been a renewed interest in X-ray emission spectroscopy (XES), and also remarkable progress in experimental techniques, especially in resonant XES also known as resonant inelastic X-ray scattering (RIXS) \cite{1}. For the measurement of X-ray emission spectra high-resolution X-ray spectrometers are mandatory. Various X-ray spectrometer geometries depending on the application and energy range of interest can be employed. In comparison to a dedicated experimental setup at a particular synchrotron beamline, the von Hamos Bragg bent crystal spectrometer \cite{2} has the advantage of being relatively compact and hence suitable for transportation while preserving both high energy resolution and collection efficiency over a wide energy range from 0.55 to 16.8 keV. Thanks to the versatility of this X-ray spectrometer, measurements of X-ray emission spectra using an electron gun or a conventional X-ray source, as well as at charged particle and X-ray synchrotron beamlines is feasible. Ample data have been collected with this instrument over the last years in different areas of research in atomic physics and for the metrology of X-ray transitions (see, e.g., \cite{3–6}). Access to X-ray synchrotron radiation facilities providing intense and tunable monochromatic X-ray beams has incited new research projects. Recently, the high-resolution von Hamos Bragg crystal spectrometer was applied to X-ray emission spectroscopy studies using X-ray synchrotron radiation at the ID21 and BM5 beamlines at the ESRF. The high-resolution measurements concern the energy-dependent double photoexcitation of argon \cite{7}, the reexamination of L\textsubscript{3} and M\textsubscript{1} atomic-level widths as well as data for L\textsubscript{3}–M\textsubscript{4,5} and L\textsubscript{3}–M\textsubscript{1} X-ray transition energies of thirteen elements ranging from xenon (\(Z = 54\)) to iridium (\(Z = 77\)) \cite{8}, and the investigation of K-edge RIXS spectra of metallic manganese and several manganese oxides that is being pursued.

2. X-ray spectrometer design and characteristics

A detailed description of the von Hamos Bragg crystal X-ray spectrometer can be found in \cite{2}. In the following an outline of the spectrometer design and performance characteristics will be given.
The principal elements of the instrument are the X-ray source defined by a rectangular slit, a cylindrically bent crystal and a position sensitive detector located on the crystal axis of curvature. For a fixed position of the components, an X-ray location on the detector corresponds geometrically to a particular Bragg angle and hence to a particular X-ray energy. The von Hamos geometry permits at one positioning of the spectrometer components data collection over an energy bandwidth limited primarily by the detector length. This bandwidth varies from 30 to 300 eV. To study a greater energy interval the central Bragg angle is adjusted by translation of the crystal and correspondingly of the detector along their axes. The position of the charged-coupled device (CCD) detector is determined by means of an optical device having a precision of ±0.3 μm. With a Bragg angular domain of 24.4–61.1°, an X-ray energy range from 0.547 to 16.8 keV can be covered with six different crystals. The crystal lamine, permanently glued to aluminum blocks machined to a precise concave cylindrical surface, have a nominal radius of 25.4 cm. The target, crystal and detector are all contained in a stainless steel vacuum chamber (180 cm × 62 cm × 24.5 cm) pumped down to about 10⁻⁷ Torr. The energy resolution is typically 1–3 eV depending on the energy, the slit width and the crystal Darwin width.

X-rays are recorded with a CCD position sensitive detector 27.65 mm long and 6.9 mm high, consisting of 1024 columns and 256 rows with a pixel size of 27 μm × 27 μm and having a depletion depth of 50 μm. The detector is cooled thermoelectrically down to −70°C. The chip was manufactured at EEV (Chelmsford, Essex, CM1 2QU England). For detection of soft X-rays from below 3 keV the spectrometer will be equipped with a scientific grade back-illuminated CCD (MTE:400B camera from Princeton Instruments, vacuum head with E2V CCD 36-40) without antireflection coating, consisting of 1340 × 400 pixels and having 20 μm × 20 μm resolution. The diffracted X-rays hit the CCD and form a 2D intensity image. Since the intensity in each pixel is proportional to the deposited energy, higher-order reflections as well as background and multiple hit events can thus be rejected by setting appropriate energy windows. The data are taken in a repetitive accumulation mode, with acquisition times per frame ranging from one to hundreds of seconds. Each image corresponding to a separate acquisition is filtered and then all the images are summed. The X-ray spectrum is obtained by projection of the final 2D-image on the dispersion axis.

### 3. Near K-shell threshold argon KL satellite structures studied by XES

Direct photoionization of inner shell electrons in atoms may be accompanied by multielectron excitations through intra-atomic electron correlations. The second electron can be either ejected to the continuum (shakeoff) or promoted to an unoccupied level (shakeup). The study of shake processes provides information on electron correlations within the atom and is a signature of the breakdown of the independent electron picture. Multielectronic effects can either be investigated by photoabsorption measurements [9] or by means of observing X-ray emission spectra (see, e.g. [10,11]). In the present study high-resolution measurements of KL-L₂,₃L satellite spectra of gaseous argon were carried out. X-ray beam energies in the range from 3455 to 6540 eV were used to investigate the evolution of the K + L double excitation from threshold to saturation. For illustration the Ar KL-L₂,₃L satellite X-ray spectra for three different excitation energies are presented in Fig. 1. The satellite line shapes and their evolution with the excitation energy were analyzed with the aid of MCD (multiconfiguration Dirac-Fock) calculations.

The excitation probabilities were deduced from the fitted satellite-to-diagram line yield ratios. The determined experimental probabilities were compared to theoretical predictions based on the model of Thomas [12]. In this model the probability for either exciting or ionizing an electron from a bound core-orbital as a result of inner-shell vacancy production can be calculated from the adiabatic to the sudden regime. Separate 2p and 2s Thomas functions were employed to fit our experimental probabilities. Results are
3. Fig. 2. Evolution of the Ar KL double excitation probability with the incident X-ray beam energy. The solid lines represent the fit to the Thomas model.

represented by the solid lines in Fig. 2. From the comparison, the onset energies ($E_{\text{thr}}$) for the 2s and 2p excitations could be determined as well as the high-energy limit of the shake probability ($P_{\infty}$), and the radius $r$ of the 2p orbital in ionic Ar. For 2p excitation $P_{\infty} = 2.19 \pm 0.04\%$ and $E_{\text{thr}} = 3462 \pm 6\text{ eV}$, while for 2s excitation $P_{\infty} = 0.45 \pm 0.01\%$ and $E_{\text{thr}} = 3544 \pm 6\text{ eV}$ and $r = 0.14 \pm 0.01\text{ Å}$.

4. L3 and M1 atomic-level widths of elements 54 ≤ Z ≤ 77

In view of a lack of modern XES data on M1 level widths in the region 54 ≤ Z ≤ 77, as pointed out recently by Campbell and Papp [13], our main objective was to establish a new set of experimental M1 level widths for 54Xe, 56Ba, 57La, 59Pr, 60Nd, 62Sm, 64Gd, 65Tb, 66Dy, 67Ho, 70Yb, 74W and 77Ir. Spin-off results are reliable experimental data concerning the L3 level widths and L3–M5 and L3–M1 X-ray transition energies for the thirteen investigated elements. Measurements of the L3–M5 and L3–M1 fluorescence X-ray lines of elements 54 ≤ Z ≤ 77 were performed with the high-resolution von Hamos spectrometer installed at both ID21 and BM5 beamlines at the ESRF in order to cover the required photon excitation energy range. The energy calibration of the spectrometer and the instrumental resolution was performed by measuring the Kα1 X-ray lines of several 3d metals with 20 ≤ Z ≤ 32. The X-ray spectra were fitted employing Voigt profiles and keeping fixed the Gaussian instrumental broadening.

Since M radiative yields are small and in addition L3M5 double vacancy states may be created through L1L2N and L3L4N CK transitions or N-shell shake processes following the L1-subshell photoionization resulting in nonradiative broadening of L3 X-ray lines, the use of an intense and tunable monochromatic X-ray beam is crucial. Photons whose energy is bigger than the L3 edge but smaller than the L1,2 edges can circumvent the unresolved N-satellites originating from L1,2L3N CK transitions. Similarly, N-shell shake processes can be suppressed by using energies below the threshold energy for double L3 + N excitation.

The L3 level widths of the investigated elements were determined from the differences between the measured linewidths of L3–M5 transitions and the M5 level widths quoted in [13]. The M1 levels were determined from the observed widths of L3–M1 transitions, employing for the L3 widths the values from the present work. A precision of 3–6% was achieved, except for Ho and Yb where the total errors were comprised between 13 and 15%. A significant improvement was thus obtained with respect to the precision of the recommended values of Campbell and Papp (14–18%). Outside the lanthanide region a shift of about $−2\text{ eV}$ was, however, observed between the two studies. In addition, in the lanthanide region, the M1 level width follows a resonance curve which is not reported in [13]. The $Z$-dependence of the M1 widths is related to the value of the total spin of the open 4f subshell and the exchange interaction with the 3s hole. The M1 level width versus atomic number $Z$ is depicted in Fig. 3.

5. 3p–1s Mn RIXS spectra of manganese oxides

Recently, a RIXS study of manganese oxides was undertaken with the intention to extend it to manganese oxide compounds (manganites) that have attracted a lot of attention in the last years [1,20].

High-resolution measurements of RIXS spectra of metallic manganese and manganese oxides such as MnO, MnO2,
Mn$_3$O$_4$ and Mn$_2$O$_3$ using X-ray synchrotron radiation were performed. By tuning the incident photon energy across the K-edge (6.539 keV) of Mn different intermediate states can be probed. For illustration, the evolution of the Mn O RIXS spectra with the incident energy, reflecting radiative transitions from specific intermediate states determined by the incident photon energy to final states, is depicted in Fig. 4. The variation in position, yield and profile of the Mn K\textit{y} X-ray emission lines and the RIXS spectra depend on the oxidation and the spin states of the Mn sites as well as on d-electron correlation and inter-atomic hybridization. A comparison to theoretical predictions could bring further insight into intra-atomic multiplet coupling, electron correlation and inter-atomic hybridization. Since in transition metal compounds, the electron correlation strength is intermediate between semiconductors and rare-earths systems, these materials represent an interesting regime to study the interplay between the itinerant and local character of 3d electrons.

6. Concluding remarks

The main objective of the presented review of the X-ray emission studies performed with the von Hamos bent crystal Bragg X-ray spectrometer at an X-ray synchrotron radiation facility, was to illustrate its potential in XES and RIXS studies. The high-resolution in a wide energy range and versatility of the instrument in combination with X-ray synchrotron radiation represents a powerful tool in the metrology of X-ray transitions and in understanding electronic structure. Further projects are foreseen in the field of XES and RIXS.

Acknowledgements

This work was supported by the European Synchrotron Radiation Facility (ESRF) and the Swiss National Science Foundation.

References