

EXPERIMENTAL RESOLUTION IN SOFT X-RAY MONOCHROMATORS

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In order to facilitate the quantitative estimation of monochromator instrument functions, we present series of X-ray absorption spectra which have been broadened with different Gaussian and Lorentzian functions. These permit assessment of the instrumental broadening at ~ 510 , ~ 710 and ~ 850 eV. We illustrate the use of our curves with X-ray absorption spectra from grating monochromators and also from double crystal monochromators, fitted with beryl and multilayer/KAP and multilayer/multilayer pairs as the dispersive elements.

1. Introduction

The purpose of this work was to investigate simple empirical methods to estimate the resolution of soft X-ray monochromators for synchrotron radiation. We expect these methods to be applicable to the soft X-ray monochromators which are increasingly finding use for X-ray absorption (XAS), extended X-ray absorption fine structures (EXAFS), X-ray photoemission spectroscopy (XPS), etc. utilising synchrotron radiation.

In general XAS, EXAFS and XPS spectra are a fold of the shape of the monochromator output, the Lorentzian broadening due to the core hole lifetime, and the spectral function which contains the required information. (In XPS there is also a contribution from the electron energy analyser.) It is the first of these quantities, the instrument function of the monochromator, which is of interest here. Various approaches are used in the literature to measure the monochromator instrument function; for instance for double crystal monochromators an upper limit for the resolution can be determined from the measured rocking curves [1,2]. Another approach is to measure the full width at half maximum (FWHM) of a known peak in the XAS spectrum (e.g. the Ne 1s or La 3d peaks) and subtract the intrinsic peak width. If the intrinsic lineshape is well known this procedure should yield the FWHM of the instrument function [3–5]. Another criterion sometimes

used is to consider the 10–90% energy width of a steplike feature.

In our own work on developing new monochromators and dispersive elements (see e.g. refs. [1,4,6,7]), and in simply measuring XAS data, we have frequently found these methods unsatisfactory. The above methods are either based on unreliable assumptions, or are complicated to perform. In practice, frequent changes of beam position and size in synchrotron storage rings, and the requirement to change spectral regions frequently preclude a complete study of the monochromator instrument function. Indeed it is often not even cost effective to completely optimise the monochromator performance because of the short times available for experimentation. There is thus a definite need for a simple, reproducible method for day-to-day use on synchrotrons where the beam dimensions and position may change quite frequently, or where one needs to measure the performance of new optical elements at a variety of energies.

In response to this need we have investigated methods based on comparison of XAS spectra of the $L_{2,3}$ edges of the 3d transition metals, measured in a simple total yield mode, with standard spectra which have been broadened to simulated the various possible instrument functions. These measurements only require a channeltron and a method for cleaning the sample surface and can be easily performed in a standard UHV apparatus. As references we use high resolution electron energy loss (HREELS) spectra [8] because these seem to be amongst the best and most reliable spectra at present available in the range of 500–1000 eV [9]. In the soft

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X-ray energy range, HREELS spectra give the same information as XAS, as long as the conditions in HREELS are chosen to analyse only losses with low momentum transfer so that the small angle approximation is valid [10,11]. We will discuss here the influence of two different instrumental broadening functions, i.e. Lorentzian and Gaussian, and present data in a form suitable for use by others.

2. Simulation of the instrumental broadening

A Gaussian curve has the form

$$I(E) = I_0(E_0) \exp\left[-(E - E_0)^2 / 2\sigma^2\right],$$

where I is the intensity and E_0 is the energy of the peak centroid. In the literature it is common to designate broadenings by the FWHM which is 2.354σ . When two Gaussian curves are folded the values of σ and FWHM add quadratically, i.e.

$$\sigma_{\text{tot}} = (\sigma_1^2 + \sigma_2^2)^{1/2}$$

or

$$\text{FWHM}_{\text{tot}} = (\text{FWHM}_1^2 + \text{FWHM}_2^2)^{1/2}.$$

The Lorentzian lineshape has the form

$$I(E) = I_0(E_0) \Gamma_L / [(E - E_0)^2 + \Gamma_L^2],$$

so that the FWHM is 2Γ . In contrast to the Gaussian curves, the widths of folded Lorentzian curves add arithmetically.

There is no simple formula for folding together Gaussian and Lorentzian broadening and they must be folded numerically in order to form the curves sometimes known as Voigt profiles [12]. In the following account we restrict ourselves to consideration of pure Gaussian or Lorentzian broadening.

We numerically broadened the HREELS spectra, which acted as our standards, with Gaussian or Lorentzian broadening functions. To test both our programs and the computer simulations of the HREELS instrument function, we took two EELS spectra of Fe. For these spectra the resolution (FWHM) was determined by Fink et al. to be 0.2 eV [13] and 0.6 eV [8]. The 0.2 eV resolution spectrum was convoluted to get a broadened EELS spectrum with a total resolution of 0.6 eV. The match between the broadened EELS spectrum and the recorded spectrum with the 0.6 eV resolution was perfect, proving that the instrumental function of the EELS spectrometer indeed is a Gaussian. It is important to know the instrumental contribution to the standard spectra because it will contribute to all our simulated spectra.

For this paper, we selected the three transition metal $L_{2,3}$ XAS spectra with the sharpest features and which

gave the best results in determining the resolution. Figs. 1, 2 and 3 show the original EELS spectra (bottom of the drawing) and curves with different broadenings (solid lines) of V, Fe and Ni respectively. The numbers on the right in the drawings are the total Gaussian broadenings (FWHM in eV) of the curves. The vanadium EELS spectrum (fig. 1) consists of two peaks, the L_3 and L_2 absorption edges, the L_3 peak having a shoulder on the low energy side. The onset of the broadening starts at an energy of 511.7 eV. As the broadening is increased (going up in fig. 1), the shoulder is no longer noticeable in the spectrum. The appearance of the shoulder is a good indication for the resolution in the range of 0.2–1.0 eV (FWHM) and makes V our first choice for characterizing high resolution monochromators. It is also clear that the relative heights of the two peaks changes for different total Gaussian broadenings. This is because the L_3 lifetime broadening is less than for L_2 . Thus it loses height more quickly when an extra, instrumental, broadening is added. This change in relative height would be a good guide for determining the energy resolution between 1.0 eV and approximately 4.0 eV, but is extremely dependent on the background slope. This indication is thus unreliable. In this resolution range it is better to compare the overall shape of the L_3 peak with the standard spectra in fig. 1. We also see that the apparent peak separation decreases at poorer

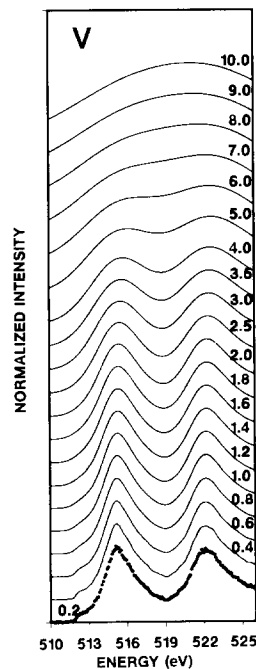


Fig. 1 Dotted curve the V $L_{2,3}$ EELS spectrum [13] with instrumental broadening of 0.2 eV FWHM. Solid lines: the same spectrum with extra Gaussian broadening. The numbers on the right give the total Gaussian broadening (FWHM).

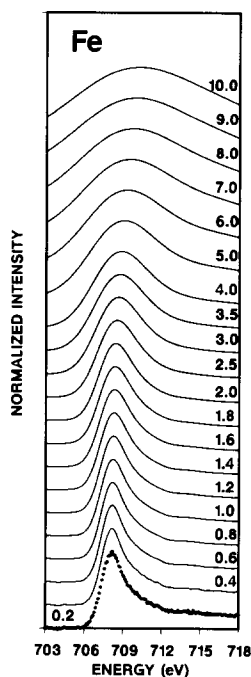


Fig. 2. Dotted curve: the Fe L_3 EELS spectrum [13] with instrumental broadening of 0.2 eV FWHM. Solid lines: the same spectrum with extra Gaussian broadening. The numbers on the right give the total Gaussian broadening (FWHM).

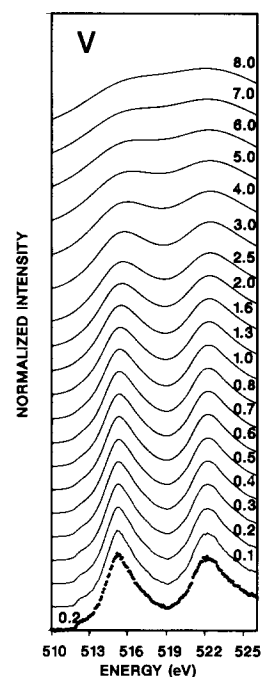


Fig. 4. Dotted curve: the V $L_{2,3}$ EELS spectrum [13] with instrumental broadening of 0.2 eV FWHM. Solid lines: the same spectrum with extra Lorentzian broadening (FWHM) as shown by the numbers on the right.

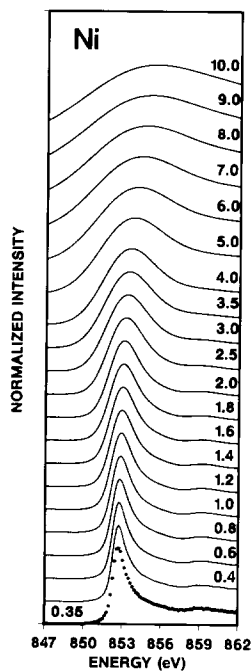


Fig. 3. Dotted curve: the Ni L_3 EELS spectrum [13] with instrumental broadening of 0.35 eV FWHM. Solid lines: the same spectrum with extra Gaussian broadening. The numbers on the right give the total Gaussian broadening (FWHM).

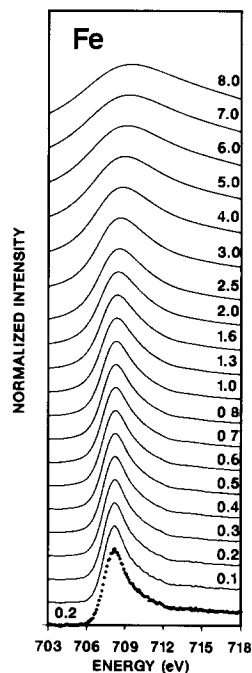


Fig. 5. Dotted curve: the Fe L_3 EELS spectrum [13] with instrumental broadening of 0.2 eV FWHM. Solid lines: the same spectrum with extra Lorentzian broadening (FWHM) as shown by the numbers on the right.

energy resolutions. At a total Gaussian broadening of approximately 8.0 eV only a single broad feature is seen.

Because of the larger spin-orbit splitting in the Fe and Ni spectra (figs. 2 and 3), we show only the L_3 peaks. The Fermi level (or XAS threshold) is at 706.6 eV in the Fe EELS spectrum and at 851.9 eV in the Ni spectrum. At the bottom both figures show the original EELS spectrum of the L_3 absorption edge which consists of an asymmetric peak with a steep edge on the low energy side. This edge shifts on broadening towards higher energies, becomes less pronounced, and is a fine indication of the resolution. In comparing the experimental spectra with the reference spectra we also considered the total FWHM of the L_3 peak. These give a good indication of the experimental resolution only up to a total energy resolution of approximately 3.5 eV for Fe and Ni, because at poorer resolutions there are some scaling problems. As seen in figs. 2 and 3 at poor resolutions the low energy end of the broadened spectra are cut by the frame of the figure before they fall of to zero intensity.

The effects of applying a Lorentzian broadening to the $L_{2,3}$ XAS spectra of V, Fe, Ni are shown in figs. 4, 5 and 6, where the numbers on the right hand side give only the FWHM of the Lorentzian broadening applied (exclusive core hole lifetime broadening). At first sight

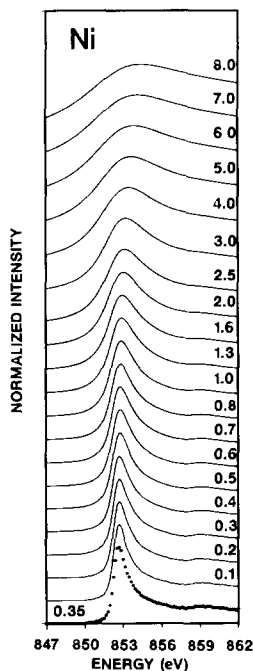


Fig. 6. Dotted curve: the Ni L_3 EELS spectrum [13] with instrumental broadening of 0.35 eV FWHM. Solid lines: the same spectrum with extra Lorentzian broadening (FWHM) as shown by the numbers on the right.

the observed trends are rather similar to those found for Gaussian broadening. However, closer examination reveals some differences. In particular the long tail of the Lorentzian function causes small details in the wings of a peak to become less distinct with smaller broadening than for Gaussian curves. This may be seen if, for instance, the 511.7 eV shoulder at 0.4 eV Lorentzian broadening is compared with that at 0.8 eV Gaussian broadening. Also Lorentzian broadening is noticeable in the relative heights of the L_2 and L_3 peaks sooner than for Gaussian broadening. Note, for instance that the two maxima have equal height at ~ 0.3 eV Lorentzian broadening or 0.8 eV Gaussian broadening. However, as we shall see below, it is not always easy to distinguish experimentally a Lorentzian machine function from a broader Gaussian function.

3. Experimental

The broadened EELS data were compared with XAS data recorded with several monochromators. The SX700 grating monochromator (10–2000 eV) at BESSY in Berlin was used for the L_3 edges of Sc to Ni. The resolution of this monochromator depends critically on the exit slit and the source beam stability. The spectra were recorded with an exit slit of 10 μm and a 1200 lines/mm grating. Optical design, performance and operation of this monochromator is discussed by Petersen [14–16]. Very recently – and after the data discussed here were taken – performance has been strongly further improved by the replacement of the old SX700 elliptical focussing mirror (tangent error 3 arcsec) by a new one (tangent error 0.92 arcsec [17]).

We also used XAS data recorded with the SOXAFS monochromator (Daresbury, UK), and with the KMC double crystal monochromator (BESSY, Berlin, Germany). Both monochromators were equipped with either two beryl crystals (for use above ~ 800 eV) and a multilayer/KAP (ML/KAP) combination (for use above ~ 600 eV). In the latter configuration the second order reflection of the multilayer was used as a band-pass filter for the KAP, as discussed in refs. [4,18]. The matched multilayers consisted of 200 double layers of W and Si ($2d = 53.2$ Å, Ovonic Synthetic Materials). In Daresbury and BESSY experiments with a combination of two multilayers consisting of 181 layers of Ni and C of 22 Å thickness (supplied by FOM-Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands) were also performed. More information on these experiments can be found in refs. [6,7].

4. Comparison with experiment

The XAS spectrum of vanadium, recorded with the SX700 grating monochromator, is shown in fig. 7, to-

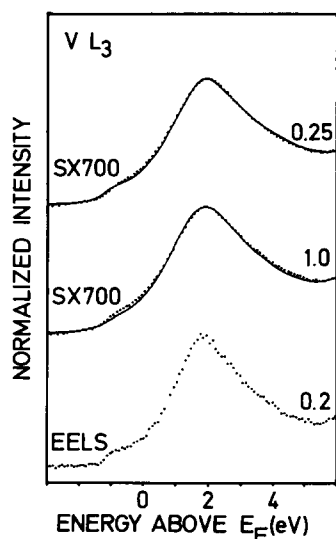


Fig. 7. V EELS spectrum (bottom curve) and the V XAS spectrum recorded with the SX700 grating monochromator (middle and upper dotted curve). The solid lines through the curves are the broadened EELS spectra with respectively Gaussian broadening (middle curve, total FWHM 1.0 eV) and with Lorentzian broadening (upper curve, Lorentz contribution of 0.25 eV FWHM).

gether with the EELS spectrum. The lines through the SX700 spectra are the broadened EELS curves which give the best match (see also table 1). Only the L_3 peak of the vanadium spectrum is taken into consideration, because the (small) uncertainty in the background in EELS spectra results in large uncertainties in the L_2 range.

An EELS curve with a total Gaussian broadening of 1.0 eV (FWHM) gives a good match for the overall width of the line (middle curve in fig. 7). But as seen from the figure the valence band structure at the shoulder of the L_3 peak is poorly reproduced. One can

Table 1

"Best" values for the FWHM of Gaussian and Lorentzian instrumental broadening function (in eV) under various conditions.

Monochromator	Energy (eV)	Gauss FWHM	Lorentz FWHM ^{a)}
Beryl/beryl	~ 850	0.85	0.2
Grating	~ 510	1.0	0.25
Grating	~ 710	1.6	0.9
Grating	~ 850	1.15	0.6
ML/KAP	~ 710	1.6	0.9
ML/KAP	~ 710	1.9	1.3
ML/ML	~ 710	6.8	6.0

^{a)} With a Gaussian contribution of between 0.2 and 0.35 eV from the EELS measurements (see text).

clearly see that the instrumental broadening function should have more a tail character. In the top curve of fig. 7 a Lorentzian broadening function of 0.25 eV (FWHM) was taken, which means that the total FWHM of the resulting broadening function, including the $V L_3$ lifetime broadening, is 0.35 eV. Although the match is not entirely perfect, it is better at the shoulder of the L_3 peak. This suggests that the instrumental function of the monochromator cannot be represented with a pure Gaussian in this case. Note that the FWHM found with a Lorentzian broadening (total FWHM 0.35 eV, of which 0.25 eV is from the Lorentzian broadening) is much smaller than the Gaussian FWHM (1.0 eV) needed for the best simulation.

Fig. 8 shows the XAS data for Fe together with the broadened EELS curves (solid lines). For the ML/KAP and ML/ML data as well as for the SX700 data we do get a good match with just a Gaussian broadening. The numbers on the right in the drawing show the FWHM (in eV) of the total Gaussian broadening of the EELS curves. The match between the broadened EELS curve and the ML/ML data fails at the end of the spectrum (top curve in fig. 8) because the contribution of the L_2 edge has been neglected.

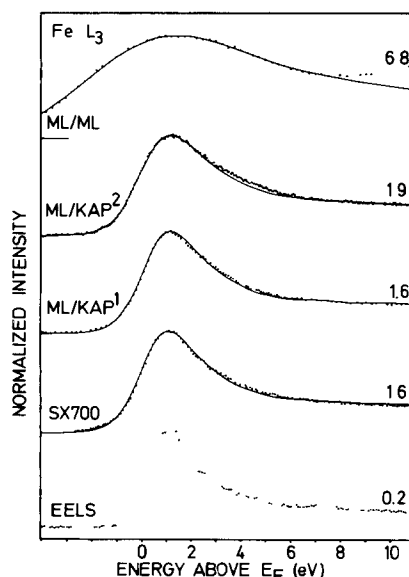


Fig. 8. The dotted curves are, from the bottom to the top: the original Fe EELS spectrum with 0.2 eV (FWHM) resolution, the Fe XAS spectrum recorded with the SX700 grating monochromator, the Fe XAS spectra recorded with the Daresbury SOXAFS monochromator (ML/KAP¹) and the KMC double crystal monochromator (ML/KAP²) equipped with a ML/KAP combination and a Fe XAS spectrum recorded with the SOXAFS monochromator equipped with a ML/ML combination. The solid lines through the spectra are the Gaussian broadened Fe EELS curves. The numbers on the right give the total Gaussian broadenings (FWHM) of these curves in eV.

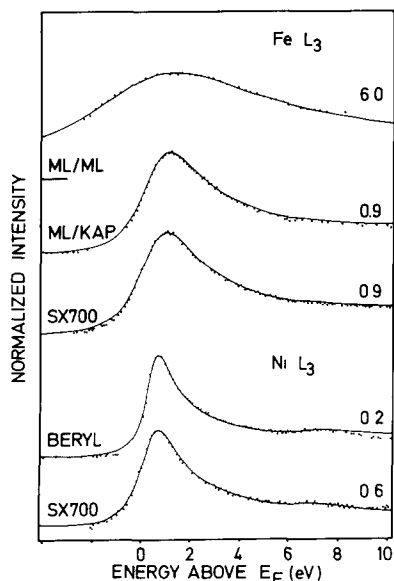


Fig. 9 Fe XAS spectra (upper three dotted curves) recorded with the SX700 monochromator and the Daresbury SOXAFS monochromator equipped with a ML/KAP and a ML/ML combination. Ni XAS spectra (lower two dotted curves) recorded with the SX700 monochromator and the Daresbury SOXAFS monochromator equipped with two beryl crystals. The solid lines are the corresponding Lorentzian broadened EELS curves. The numbers on the right give the Lorentzian broadenings (FWHM) of these curves (in eV) added to the original Gaussian instrumental FWHM of the standard EELS spectra.

Because of the good results for Lorentzian broadening for the XAS data of V, we tried also Lorentzian broadening on the Fe EELS spectra, but it clearly resulted in a poorer match, as shown in fig. 9 for some data on Fe and Ni.

The XAS data for Ni recorded with the SX700 and double beryl monochromators are shown in fig. 10. Again the match between the Gaussian broadened EELS curves and the XAS data is very good and again the match with Lorentzian broadened EELS curves (fig. 9) is less perfect.

5. Discussion

As illustrated in figs. 7–10, a given measured spectrum can often be simulated rather well using standard data and either Gaussian or Lorentzian approximations to the soft X-ray monochromator instrument function. As seen in table 1, the assumption of Lorentzian broadening gives much more attractive figures for the resolution than Gaussian broadening, particularly at good resolution. For this reason alone we think that Lorentzian figures are likely to be more widely quoted.

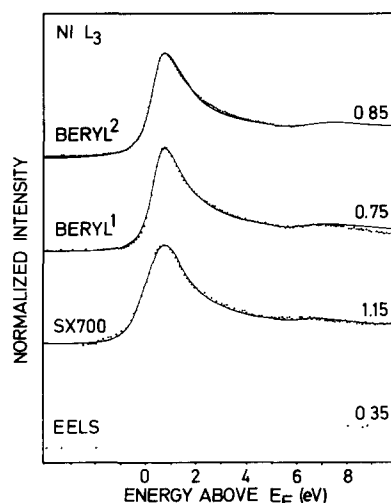


Fig. 10. Ni EELS spectrum (bottom curve) with 0.35 eV resolution (FWHM) and the Ni XAS spectra (dotted curves) recorded with the SX700 grating monochromator, the SOXAFS monochromator (Beryl¹) and the KMC double crystal monochromator (Beryl²) equipped with beryl crystals. The solid lines through the XAS spectra are the Gaussian broadened Ni EELS spectra. The numbers on the right in the drawing are the total Gaussian broadenings (FWHM) of these spectra, in eV.

Whilst some theoretical arguments can be made in favour of Gaussian instrument functions, in practice there is probably no good reason to assume either pure Gaussian or pure Lorentzian forms and an infinite number of shapes are feasible. The results reported here show that it is not usually possible to determine unambiguously the instrument function of a soft X-ray monochromator by comparing measured XAS spectra with broadened, standard data. We do not believe that methods based on deconvolution would be superior.

We note that whilst our studies did not yield detailed instrument functions, figs. 1–6 were a basis for a reliable and reproducible scale of resolution for several different monochromators. We regard this as very useful in view of the numerous inconsistencies in quoted instrumental resolutions, revealed by even a short study of the XAS and synchrotron PS literature. We were able to show that the instrument function of a high energy grating monochromator in standard (not optimal) operation not only increases in width at higher energies, but that it also changes shape from run to run. This is the reason why the SX700 resolution given for 710 eV appears anomalously bad (see table 1). At ~ 500 eV the Gaussian function had insufficient weight in the tail to provide an ideal simulation.

It is interesting that the XAS spectra obtained with artificial multilayers as the dispersive elements in the monochromator are so well fitted with Gaussian broad-

ening. There are arguments that the contribution of the crystal rocking curve should give a Gaussian contribution to the instrument function. Clearly if this contribution is very large, then possible non-Gaussian contributions from aberrations in the optical system can be neglected.

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References

- [1] G. van der Laan, J.B. Goedkoop, J.C. Fuggle, M.P. Bruijn, J. Verhoeven, M.J. van der Wiel, A.A. MacDowell, J.B. West and I.H. Munro, *Nucl. Instr. and Meth.* A255 (1987) 592.
- [2] Z. Hussain, E. Umbach, D.A. Shirley, J. Stöhr and J. Feldhaus, *Nucl. Instr. and Meth.* 195 (1982) 115.
- [3] H. Maezawa, S. Nakai, S. Mitani, H. Noda, T. Namioka and T. Sasaki, *Nucl. Instr. and Meth.* A246 (1986) 310.
- [4] G. van der Laan, J.B. Goedkoop and A.A. MacDowell, *J. Phys.* E20 (1987) 1496.
- [5] F.J. Himpsel, Y. Junget, D.E. Eastman, J.J. Donelon, D. Grimm, G. Landgren, A. Marx, J.F. Morar, C. Oden, R.A. Pollak and J. Schneir, *Nucl. Instr. and Meth.* 222 (1984) 107.
- [6] A.A. MacDowell, J.B. West, G.N. Graves and G. van der Laan, *Rev. Sci. Instr.* 59 (1988) 843.
- [7] J. Feldhaus, F. Schäfers and W. Peatman, *Proc. SPIE* 733 (1987) p. 24.
- [8] J. Fink, private communication.
- [9] J. Fink, Th. Müller-Heinzerling, J. Pflüger, A. vom Felde and B. Scheerer, *Proc. Int. Conf. on X-ray and Inner-Shell Processes in Atoms, Molecules and Solids*, eds. A. Meisel and J. Finster (Karl-Marx-Universität, Leipzig, GDR, 1884), p. 425.
- [10] R.D. Leapman, L.A. Grunes and P.L. Fejes, *Phys. Rev.* B26 (1982) 614.
- [11] M. Inokuti, *Rev. Mod. Phys.* 43 (1971) 297.
- [12] H.H. Voigt, *Abriss der Astronomie I*, Bibliographisches Institute AG (Manheim, 1969).
- [13] J. Fink, Th. Müller-Heinzerling, B. Scheerer, W. Speier, F.U. Hillebrecht, J.C. Fuggle, J. Zaanen and G.A. Sawatsky, *Phys. Rev.* B32 (1985) 4899.
- [14] H. Petersen and H. Baumgärtel, *Nucl. Instr. and Meth.* 172 (1980) 191.
- [15] H. Petersen, *Opt. Commun.* 40 (1982) 402.
- [16] H. Petersen, *Nucl. Instr. and Meth.* A246 (1986) 260.
- [17] K. Becker and K. Beckstette, *Proc. Int. Conf. for Ultra High Precision Technology*, Aachen, May 1988 (Springer, 1988) p. 212.
- [18] G. van der Laan, M.P. Bruijn, J.B. Goedkoop and A.A. MacDowell, *Proc. SPIE* 733 (1987) p. 38.