

J. Synchrotron Rad. (1999), **6**, 179–181

High-energy X-ray absorption spectroscopy at ESRF BM29

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The availability of third generation synchrotron sources now allows the routine performance of EXAFS investigations using K absorption edges occurring above 30 keV. Measurements made at absorption edges in the energy range 40 keV to 70 keV using the EXAFS beamline BM 29 of the ESRF have demonstrated a great potential for high resolution structural studies. The effect of the core-hole lifetime broadening, though apparent, is found to be manageable if high quality data are acquired over the large k -range accessible for heavy element K absorption edges. Examples are presented for the Eu K-edge and the W K-edge, demonstrating clear advantages for structural investigations over those conventionally performed at the L_{III} absorption edge.

Keywords: EXAFS; core-hole lifetime broadening; 3rd generation synchrotrons.

1. Introduction

Extended X-ray absorption fine structure (EXAFS) spectroscopy as a dedicated tool to determine short range inter-atomic structure, has in general previously been confined to absorption edges below 30 keV. (A typical upper value for the useful photon energy of bending magnet beamlines on most second generation synchrotron sources.) The limitation in available photon energy at older synchrotrons has to some extent been circumventable since the absorption fine structure of elements with K-edges beyond 30 keV is accessible via their L_{III} edge. However, the presence of the L_{II} absorption edge, that typically occurs a few hundred electron volts higher in energy, tends to restrict the range of signal that may be used in an EXAFS analysis and consequently there is a reduction in the accessible information content when compared with K-edge data.

Data collected at a K absorption edge are most commonly limited by the signal to noise ratio attainable with an EXAFS spectrometer. The European Synchrotron Radiation Facility (ESRF) is a third generation high energy synchrotron that typically operates with a storage ring energy of 6 GeV and with ring currents of 200 mA. Bending magnet beamlines such as the EXAFS spectroscopy beamline, BM 29, consequently operate at a much higher critical energy than those at most second generation synchrotron sources *c.f.* E_c for a ESRF bending magnet is 19.15 keV whilst for the bending magnet stations of the 1.8 GeV positron ring of LURE DCI (Orsay, France) is 3.62 keV.

Some older synchrotron sources do operate to give high critical energies for their bending magnet beamlines, for example HASYLAB, which operates with a ring energy of 4.5 GeV and has a bending magnet critical energy $E_c = 16.6$ keV. This is achieved through having a small bending radius (12.2 m for HASYLAB, in contrast to 25 m for the ESRF). However, to date little use was made of this capability at second generation sources apparently for two principle reasons. These are:

1. There was, and still is, a degree of opinion that EXAFS is unable to give significant structural information at K-edges of higher Z elements due to the short lifetime of the excited atomic state. This causes a damping and broadening of the signal which in particular affects the high frequency components of the measured signal and consequently reduces the sensitivity of the technique to the longer range inter-atomic distance correlations.
2. The inability of spectrometers based at older sources, to measure EXAFS spectra with sufficiently high signal to noise ratios so as to allow the extraction of the structural information, or in some cases even make visible the heavily core-hole lifetime damped signal. This can largely be attributed to a combination of limits arising from photon flux and intrinsic machine stability.

The latter reason is perhaps the more significant as to why high energy studies were not pursued previously at second generation sources, although this fact is difficult to corroborate.

The aim of this paper is to show the feasibility of EXAFS at high energy K-edges up to $E \approx 75$ keV, and also to underline the significant potential for such studies.

2. Experimental

Data have been collected for metals, oxides and carbides of various elements of the lanthanide series and for tungsten. Here we report on the Eu_2O_3 and WC systems as model examples providing high energy spectra. All data were taken at the ESRF-BM 29 spectrometer (Borowski, Filipponi, Loeffen, 1998). This instrument is built onto an ESRF bending magnet with the aforementioned characteristics and is equipped with an ultra stable fixed exit two crystal monochromator.

The data were measured in transmission geometry and over a temperature range of 20 K to 300 K using a pair of flat Si(511) monochromator crystals and operating the monochromator with 10 to 20 % detuning (in units of the width of the monochromator rocking curve), from the peak intensity. For Eu_2O_3 , data were also collected using Si(311) crystals for comparison. The accessible energy range of the crystals are given in table 1. The Si(311) and Si(511) data sets were found to be completely superposable up to $k \approx 22 \text{ \AA}^{-1}$. The Si(311) crystal set gives slightly better statistics due to the higher flux with respect to the Si(511) crystals, but differences were observed in the high energy/high k region of the spectra. These effects were found to be due to operating at the limit of the angular range of the BM 29 monochromator. This observation illustrates that when operating at high energies with low order cut monochromator crystals (that necessitate small incidence and reflection angles), their alignment is particularly critical. For the studies presented here, the Si(511) monochromator crystals allowed us to operate reliably over the required angular range, and instrumental artifacts were thus avoided.

Table 1
Parameter of the Monochromator crystals

Crystal type	Accessible energy range (keV)	Data
Si (311)	6 - 50	Eu_2O_3 †
Si (511)	10 - 75	WC, Eu_2O_3

† data taken for comparison with Si(511), see text.

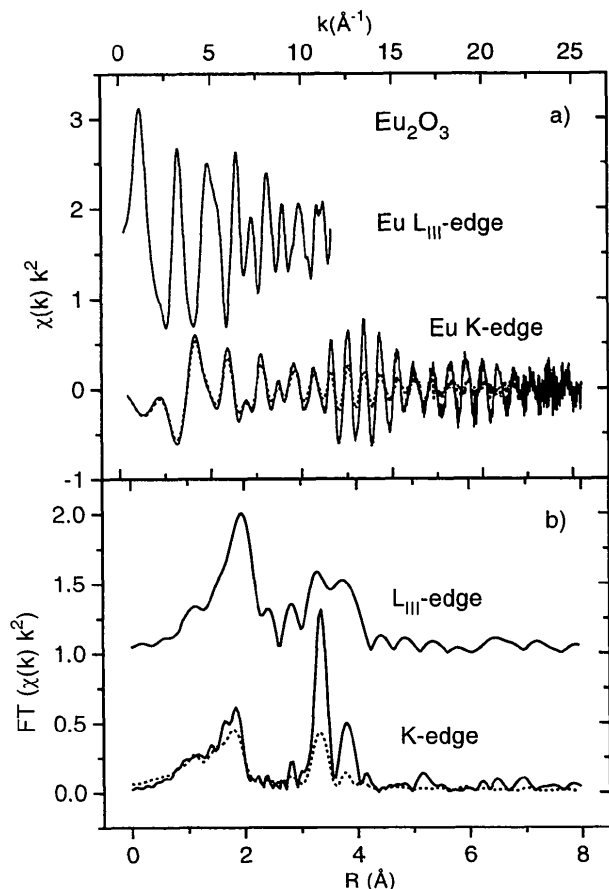


Figure 1

a) Comparison of the EXAFS ($\chi(k)k^2$) of Eu_2O_3 at the Eu L_{III} ($E_0 = 6977$ eV, $\Gamma = 3.91$ eV) and K absorption edge ($E_0 = 48518$ eV, $\Gamma = 21.0$ eV) (energies from: Bearden & Burr, 1967; core level width from: Krause & Oliver, 1979). The full lines are the measurement taken at 24 K, for the K-edge data, the room temperature data (dashed) are shown for comparison. b) The Fourier transform of the EXAFS shown resolution achieved when working at the K-edge, well below the Debye temperature, is evident (low temperature data: full lines, the room temperature data: dashed line).

Samples were commercially available high purity micrometric powder (Eu_2O_3 , WC), mixed with BN and pressed into pellets of suitable thickness for transmission absorption measurements (absorption jump $\Delta\mu x \approx 1$). Care was taken to use fresh Eu_2O_3 powder to avoid CO_2 /water contamination from air. The employed detectors were ionisation chambers, (Pettifer *et al.*, this proceedings) filled with Kr gas. The filling was chosen to optimise the signal to noise ratio of the data, through appropriately chosen absorption characteristics for the both ion chambers.

Some similar investigations in the high energy regime have also recently been performed at Spring8 (T. Tanaka, *et al.*, 1998; Y. Nishihata *et al.*, 1998). These are studies mainly focused on the absorption edge structure and position as a function of sample composition and on the core-hole lifetime effect.

Fig. 1 a) shows a comparison of the fine structure of Eu_2O_3 at $T=24$ K, probed of the Eu L_{III} and K-edge, respectively. A room

temperature spectra taken at the K-edge is shown for comparison and we will discuss the importance to perform the measurement at temperatures well below the Debye temperature below. As expected, the signal is strongly damped in the K-edge $k \approx 10 \text{ \AA}^{-1}$ due to the short core-hole lifetime corresponding to a core hole width of $\Gamma = 21$ eV, while a stronger detailed signal is obtained at the L_{III} edge ($\Gamma = 3.91$ eV)¹. In contrast, the presence of the L_{II} -edge limits the L_{III} EXAFS spectral range to around $k = 12 \text{ \AA}^{-1}$, while reliable structural information can be extracted from the corresponding K-edge EXAFS to $k \approx 25 \text{ \AA}^{-1}$ in this case.

In Fig. 1 b) we show the corresponding k^2 weighted Fourier-transform (not phase corrected) of this data. Eu_2O_3 has a complicated bixbyite structure ($Ia3$), of which the coordination shells around a Eu atom are given in Table 2. The first 3 oxygen distances cannot be resolved either in the L_{III} , or in the K-edge data. The nearest 4 Eu-Eu distances can be treated as two shells at 3.609 \AA (weighed average of shell 4 and 5 in Table 2) and at 4.114 \AA (weighed average of shell 7 and 8 in Table 2). These two shells are clearly separated in the K-edge signal, whilst such a separation is not possible with the L_{III} real-space resolution. Higher Eu shell signals can also clearly be K-edge data, when working at low temperatures. This example illustrates the gain in spatial resolution achieved when working at the K-edge in comparison with the L_{III} -edge. The reason for this is that the information is contained within the frequency and amplitude of the EXAFS. Although the core hole width is 5 times larger at the K-edge, the corresponding loss in information is largely recovered by the large k -range which extends more than a factor 2 over that of the L_{III} -edge. In addition, one is interested in the structural information which is evenly distributed in k -space, whereas the signal damping due to the core hole effect results in a constant broadening in energy space.

Table 2

Neighbouring shells in Eu_2O_3 calculated from crystallographic parameters ($u = -.033$, $x = 0.394$, $y = 0.149$, $z = 0.380$ (Wyckoff, 1986) and WC with hexagonal unit cell ($a = 2.9065$ \AA , $c = 2.366$ \AA (Wyckoff, 1982)). For Eu_2O_3 , all distances up to $R = 5.5$ \AA are shown, for WC, C-distances are only quoted for $R < 5.5$ \AA . N are the number of atoms in the shell.

shell	Eu_2O_3			WC		
	element	R (\AA)	N	element	R (\AA)	N
1	O	2.2904	2	C	2.1972	6
2	O	2.3011	2	W	2.8366	2
3	O	2.3953	2	W	2.9065	6
4	Eu	3.5971	2	C	3.6435	6
5	Eu	3.6149	4	W	4.0613	12
6	O	4.0924	2	C	4.5739	6
7	Eu	4.1031	2	C	4.6608	12
8	Eu	4.1187	4	W	5.0342	6
9	O	4.3385	2	C†	5.4192	6
10	O	4.5196	2	W	5.6732	2
11	O	4.5360	2	W	5.7784	12
12	O	4.5844	2	W	5.8130	6
13	O	4.5898	2	W	6.3744	12
14	O	4.6431	2	W	6.4682	12
15	O	4.8382	2	W	7.5848	12
16	O	5.1131	2	W	7.6899	12
17	O	5.3482	2	W	8.1226	12
18	Eu	5.4330	2	W	8.1964	24
19	Eu	5.4801	4			

†largest C-distance quoted

¹We neglect in this discussion the role of the angular momentum, which is partly responsible for the differences between the L_{III} and K-edge EXAFS (phase shift of nearly π for the low k -range). From this point of view, L_{I} data would be a better comparison, though complicated by the interference of the L_{II} fine structure.

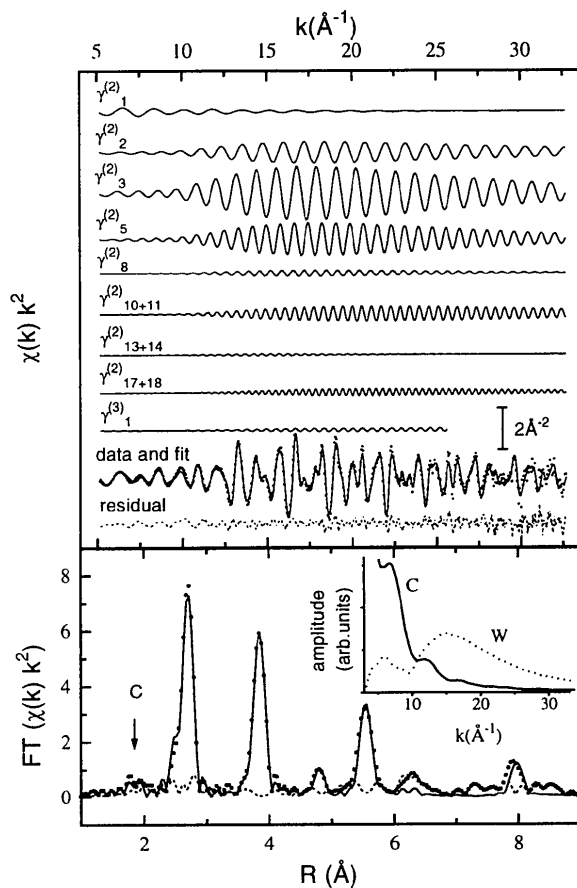


Figure 2

The upper part shows the calculated signals used for the fit. The nomenclature follows Table 2, e.g. $\gamma_1^{(2)}$ is the signal corresponding to the first shell as quoted in Table 2, $\gamma_{17+18}^{(2)}$ stands for the summed signal of shell 17 and 18. The fit (full) in k -space to the experimental data (dots) of WC at 22 K and the residual are shown (dashed). $\gamma_1^{(3)}$ is the three body contribution of the degenerate 180° triangle with a long bond of $R = 5.813$ Å. The upper value of this signal of $k \approx 26$ Å⁻¹ represents the current limitation of the analysis package. The lower part shows the resulting Fourier transform (data (dots), simulation (full) and residual (dashed)). Inset are the calculated backscattering amplitudes for carbon and tungsten, illustrating the small contribution of the light element to the spectra.

This constant energy distribution translates into a k -space interval that is proportional to the inverse of the k value,

$$\Delta k(k) = \frac{m_e}{\hbar} \frac{1}{k} \Delta E$$

and thus the core-hole lifetime broadening affects the spectra much less at higher k values. We observe that there is a small loss in intensity in the oxygen first neighbours contribution in the K-edge to the oxygen amplitude function which falls rapidly for $k > 10$ Å⁻¹, whilst that of the heavy elements like Eu extends to $k > 30$ Å⁻¹.

It is important to mention the strong influence of the lattice vibration and the related signal damping connected to the Debye-Waller factor. In Figure 1 a) and b) we compared the fine structure data and corresponding Fourier transform of Eu₂O₃ taken at the Eu K-edge at 24 K and 290 K. While the signal corresponding to the oxygen coordination distances 1 to 3 (Table 2) is only slightly affected, the amplitudes of the above discussed 2 Eu coordination shells are strongly reduced at 290 K and more distant shells are

not detected anymore. Although the gain in spatial resolution due to the large measured k -range is temperature invariant, it is very clear from this comparison that full advantage of the enhanced information contents can only be taken when working well below the Debye temperature. Although we can not discuss this point here in detail, it can be related to

- the $\exp(-2\sigma^2(R)k^2)$ like influence on the amplitude function of an atom with a Debye-Waller factor $\sigma(R)$, where R is its distance from the excited atom
- the core-hole lifetime effect on the low k -range
- the probed k -range and the signal to noise ratio

Working at low temperatures (i.e. well below the Debye temperature of the measured material) is therefore generally necessary if high spatial resolution and higher shell information are required.

One question that has been raised in connection to this previously unexploited energy domain is the validity of the present EXAFS theory, especially if relativistic corrections should play a role. A detailed discussion cannot be given here, but our last example shows the multiple-scattering analysis of WC at 20 K (K-edge, $E_0 = 69.525$ keV (Bearden & Burr, 1967)) using the GNXAS code (Filipponi, *et al.*, 1995; Filipponi & Di Cicco, 1995) without additional corrections. We used the known crystallographic structure (Wyckoff, 1982) and included only the first W-C signal (n.b. the very weak W-C signal), 7 W-W two body contributions and one three body contribution (degenerate 180° triangle). The program automatically takes the core-hole lifetime effect into account. Fig. 2 shows the excellent quality of the fit, with a signal that extends to around $k = 33$ Å⁻¹ corresponding to a scan over an energy range of 5.1 keV with an average noise level of $1.5 \cdot 10^{-4}$. The quality of this fit would suggest that current theory is sufficient.

3. Conclusion

In conclusion we demonstrate the feasibility and the power of EXAFS performed at high energy K absorption edges up to 75 keV. We highlight the influence of the Debye-Waller term is stronger than normally encountered at lower energies, making low temperature studies necessary, but consequently shows a large potential for Debye-Waller studies. High energy EXAFS investigations at the K-edge offer advantages over corresponding L edges resolution due to the large accessible k -range, if high signal to noise ratios are achieved.

References

- Bearden, J.A. & Burr, A.F. (1967). *Rev. Mod. Phys.* **39**, 125.
 Borowski, M., Filipponi, A. & Loeffen, P.W. (1998). *BM 29 handbook*, <http://www.esrf.fr/exp-facilities/BM29/handbook/handbook.html>.
 Filipponi, A., Di Cicco A. & Natoli C.R. (1995). *Phys. Rev.* **B 52**, 15122-15134.
 Filipponi, A. & Di Cicco, A. (1995). *Phys. Rev.* **B 52**, 15135-15145.
 Krause, M.O. & Oliver, J.H. (1979). *J. Phys. Chem. Ref. Data* **8**(2), 329-338.
 Nishihata, Y., Kamishima, O., Kubozono, Y., Maeda, H. & Emura, S. (1998). *J. Synchrotron Rad.* **5**, 1007-1009.
 Pettifer, R.P., Borowski, M. & Loeffen, P.F. (1998). *The Physics of Ionisation Chambers - or how to improve your signal to EXAFS Measurements*, this proceedings.
 Tanaka, T., Yamamoto, T., Yoshida, S., Mitsuda, A., Wada, H., Nishihata, Y., Tanida, H., Uruga, T. & Emura, S. (1998). *Chemical shift x-ray K-edge absorption energy for europium compounds*, this proceedings.
 Wyckoff, R.W.G. (1982). *Crystal Structures*, 2nd ed. vol 1, 150, Krieger Publishing, Malabar, Florida.
 Wyckoff, R.W.G. (1986). *Crystal Structures*, 2nd ed. vol 2, 4, Krieger Publishing, Malabar, Florida.

(Received 10 August 1998; accepted 28 January 1999)