
CONTRIBUTED PAPERS

IN-LAB. X-RAY ABSORPTION EXPERIMENTS ON MIXED VALENT MATERIALS

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I. Introduction

Mixed-valent materials present very interesting physical properties which are related to fast-charge fluctuations ($\tau_f \sim 10^{-13}$ sec) [1]. They are mainly observed on $4f$ materials, i.e. in the Rare Earth compounds (e.g. SmS under pressure, SmB₆, TmSe, YbAl₂ etc ...).

Because the characteristic time of the photoabsorption process ($\tau_f \sim 10^{-17}$ sec) is much smaller than this $4f$ fluctuation time, X-ray absorption spectroscopy (XAS) has been widely used for the study of ground state properties of these mixed-valent materials [2].

Usually XAS experiments are performed using national synchrotron facilities: DCI at LURE (France), SSRL in Stanford (USA), Chess at Cornell (USA), Photon Factory in Japan, Hasylab in Hamburg (W.-Germany), ADONE at Frascati (Italy)... However it is well-known that the access to these synchrotron facilities are quite limited and should be devoted only to studies which need absolutely the high flux delivered by the storage rings.

Because in most cases mixed-valent properties are observed in concentrated systems, the use of Bremsstrahlung Radiation delivered by a classical X-ray source may be considered. This is even more interesting since the new high-power rotating anodes generators have been developed. Our purpose is to give some conclusions on experiments we performed on an in-lab. spectrometer at LMSES, in Strasbourg.

II. Experimental Outlines

The basic conditions for a good absorption experiment are:

1. High flux source of photons/time, with a low level of harmonics;
2. High resolution in energy, particularly for the edge studies;
3. Sensitive and stable photon detection;
4. Carefully prepared samples.

II.1. Source of photons: Bremsstrahlung versus synchrotron

We used a rotating anode generator RIGAKU RU-200. It was modified at the factory in order to work under two voltage regimes: the high voltage range (20 to 60 kV) with a standard filament allowing a tube, current of 200 mA under 60 kV, and the low voltage one (5 to 20 kV) allowing 200 mA under 20 kV. This option was justified by the necessity of a low level of harmonics, specially when we study low energy edges. In the case of light Rare Earths, the L_{III} edges, in which we are interested, lie in the 5-7 keV, then second order and third order harmonics may be excited in the standard high voltage regime. The photons which don't share in the absorption process are nevertheless counted and data may be spurious. In this case, it is necessary to work in the low voltage regime in order to excite only the first order energies with rather high counting rates, because of the high tube current. The choice between either silver or molybdenum anodes, used in the laboratory because of their high atomic number, depends on the energy range on which we work: only Bremsstrahlung radiation must be used and no emission line must be present over the spectra. The photon density (photon/sec Å eV Å mrad) in the 5-15 keV range may reach 10^7 and must be compared with the 10^9 - 10^{12} obtained in the storage rings.

II.2. Spectrometer resolution

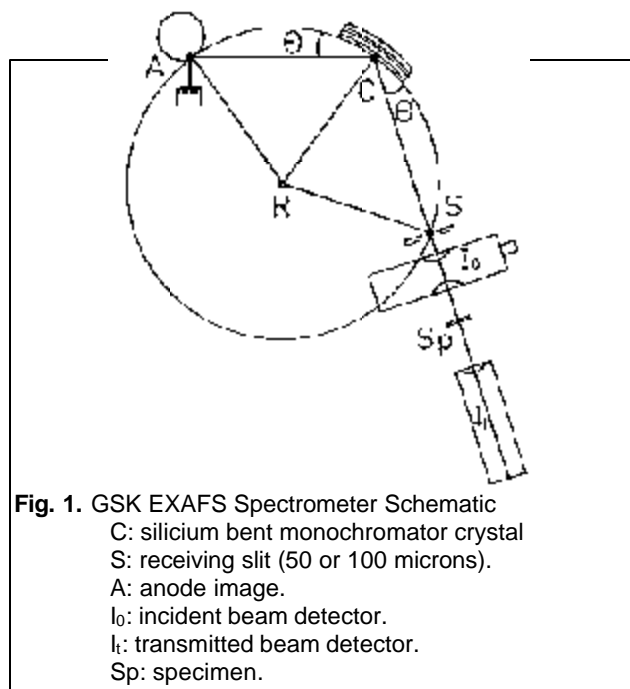
The spectrometer we have mounted on the photon source was developed by GSK Scientific [3]. Fig. 1 illustrates the principles of operation. The crystal and the slit-sample-counters-holder move together on the Rowland-Circle by mean of lead screws and computer controlled stepping motors in order to satisfy the focusing conditions in any position.

One of the six suitable silicium crystals (111), (311), (400), (511), (620), (840) can be chosen according to the energy range, the resolution and the counting rate we want. The energy range we can scan with this in-lab. facility is 3.5 to 26 keV. Energy resolution versus energy for these crystals is reported on Fig. 2.

Fig. 3 and Fig. 4 show some tests we have made on the well-known Cu K edge on a pure copper 12 microns foil, and the Cr K edge on K_2CrO_4 . As shown on these figures, the energy resolution we obtained on the in-lab. spectrometer is quite comparable to that for absorption experiments we performed with the synchrotron radiation. Obviously the counting time in the former case is much longer and the statistic is not so good. Nevertheless it appears that in the low energy range (5-9 keV) a 2 eV resolution can be achieved with the in-lab. spectrometer.

II.3. Detection

Detectors must be efficient and stable versus time and temperature because of the rather long counting



times, particularly for EXAFS spectra. We used a proportional Argon-Methane 10 counter and a scintillator I counter, both followed by energy discriminators. The counting rates lie in the 10^4 - 10^5 cps/sec. According to recent developments, it should be better to supply the in-lab. spectrometer with ion chamber counters which present a very good linearity over a large dynamic range and a lower electronic noise.

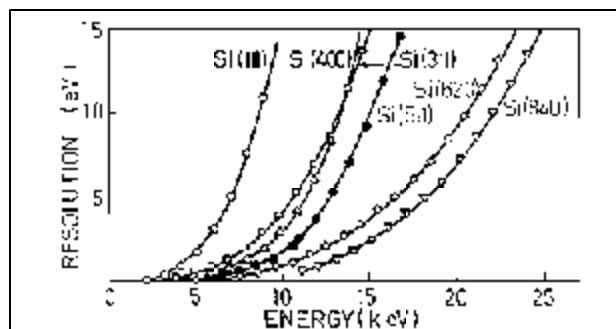


Fig. 2. Resolution versus Energy for different Monochromator Crystals.

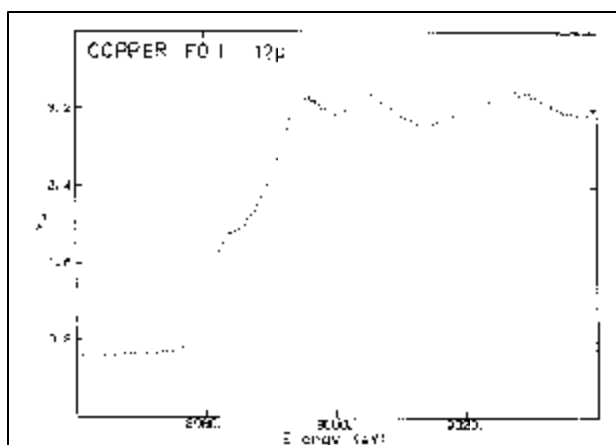


Fig. 3. K Edge of Cu on a 12 microns Copper Foil. Crystal: (511)

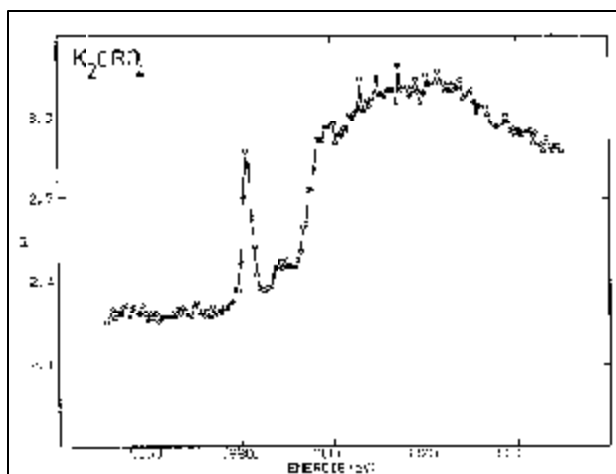


Fig. 4. K Edge of Cr on K_2CrO_4 . Crystal: (311).

II.4. Samples

Both for synchrotron and in-lab. studies, samples must be carefully prepared, without holes or inhomogeneity. They are thin foils or fine powders deposited on kapton or polycarbonate filters. Usually the absorption of the samples is measured at room temperature, however in several cases (e.g. phase transition studies, evolution of electronic configuration with temperature) it is necessary to perform low temperature experiments. The great advantage is to increase the signal/noise ratio because of the reduction of the Debye-Waller factor at low temperature. The counting times for such experiments are therefore considerably smaller and the results more accurate. The overall experimental set-up, including the helium circulating cryostat (4.2 K to 300 K) is shown on Fig. 5.

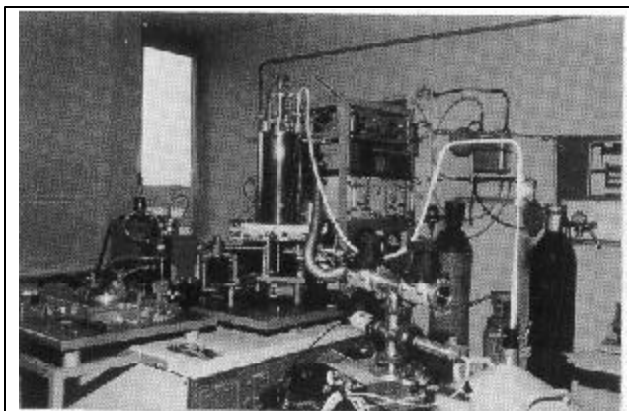


Fig. 5. The spectrometer mounted on RIGAKU RU-200, set up with a Helium Cryostat.

III. Application to the Study of Mixed-Valent Compounds

III.1. L_{III} edges: (X-Ray absorption near, Edge Structure)

Rare earth atoms are characterized by a $4f^m(5d6s)^m$ electronic configuration where, by convention, m is the valence. However the so-called anomalous Rare-Earths can be present in an intermediate-valent state due to the fluctuation between two $4f$ -configurations, for example:

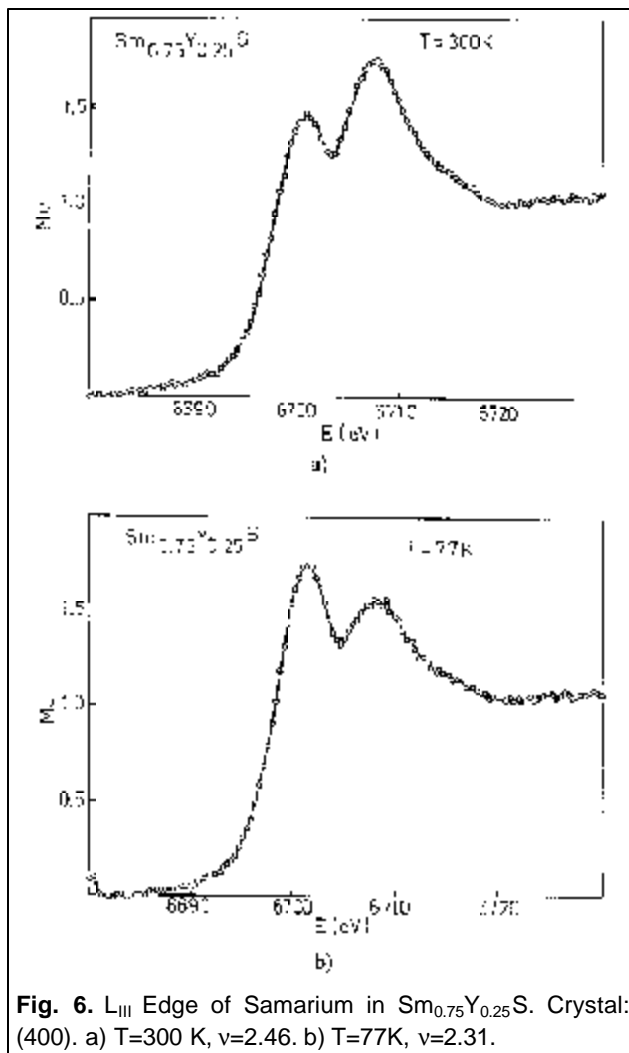
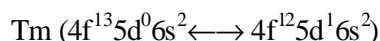
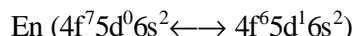
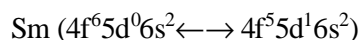
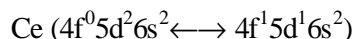


Fig. 6. L_{III} Edge of Samarium in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$. Crystal: (400). a) $T=300\text{ K}$, $\nu=2.46$. b) $T=77\text{ K}$, $\nu=2.31$.

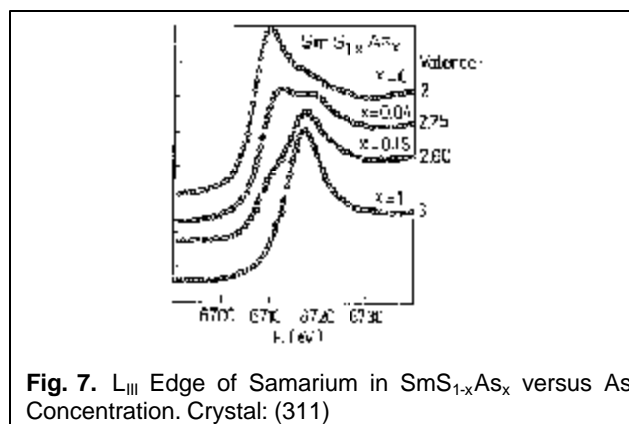
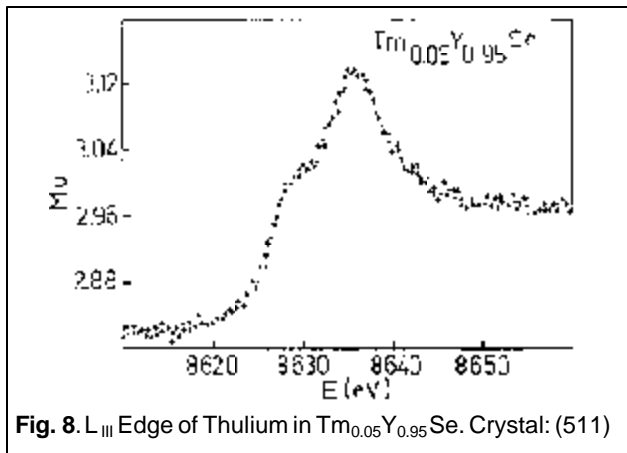


Fig. 7. L_{III} Edge of Samarium in $\text{SmS}_{1-x}\text{As}_x$ versus As Concentration. Crystal: (311)

Because the charge fluctuation time is longer (10^{-13} sec) than the photoabsorption process of the $2p_{3/2} \rightarrow nd$ transition (10^{-17} secretary), two lines corresponding to both electronic states are clearly observed on L_{III} edge spectra. Line-shape analysis of the spectra yields directly the mean value of the

valence in the absence of final state effects. As an example, we show on Fig. 6 the L_{III} absorption of samarium in the mixed-valent $Sm_{0.75}Y_{0.25}S$ compound [4] measured at $T=300$ and 77 K. The evolution of the valence with the temperature is clearly demonstrated. The spectra shown here are rough experimental data (i.e. Non-deconvoluted by the experimental resolution). The line-shape analysis of these L_{III} edges allows a highly accurate determination of the valence which is similar to that deduced from previous studies performed with synchrotron radiation [5]. We measured similar valence changes in the $SmS_{1-x}As_x$ system by changing the As-concentration (Fig. 7).

For these edge measurements the counting times are typically 30 to 60 mn in order to obtain a good statistic. Even in the case of diluted samples we have succeeded to measure L_{III} edges down to 5% atomic concentrations. This is well-shown on Fig. 8 where we reported the Tm edge in $Tm_{0.05}Y_{0.95}Se$. In this case the



counting time was 3 hours.

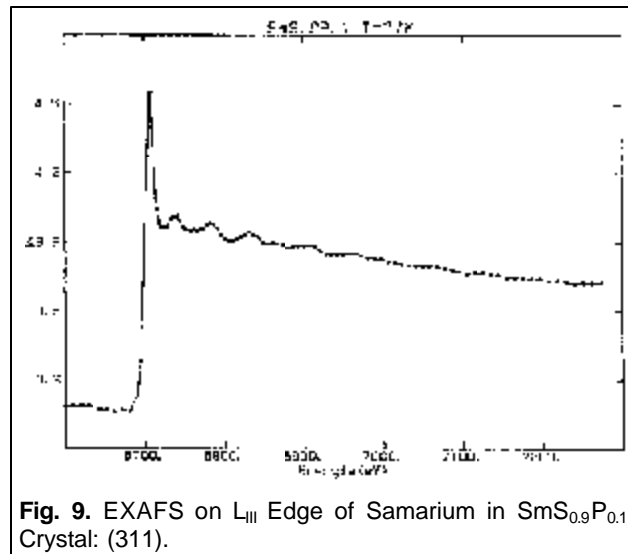


Fig. 9. EXAFS on L_{III} Edge of Samarium in $SmS_{0.9}P_{0.1}$. Crystal: (311).

III.2. EXAFS: (Extended X-Ray Absorption Fine Structure)

By analyzing the oscillations of the absorption coefficient over 1000 eV above the edge, and with an adequate mathematical treatment, it is possible to get informations on the local environment of a central atom [6]. In mixed-valent compounds the physical problem is to know if the nearest neighbours of a $4f$ fluctuating ion follows or not the breathing of the $4f$ shell. The Exafs results obtained after the L_{III} edge of the samarium in $SmS_{1-x}P_x$ compounds are shown on Fig. 9. The radial distribution function (RDF) obtained by a Fourier transform of the Exafs data are shown on Fig. 10. The first and second shell of neighbours in the NaCl type structure are clearly observed. It is then possible to isolate one of the shells by Fourier filtering, and to perform an adjustment to the experimental data by the well-known Exafs formula [7]. We show on Fig. 11 the best fit we obtained on one of these mixed-valent compounds, $SmS_{0.9}P_{0.1}$, by using a single average distance, what means here

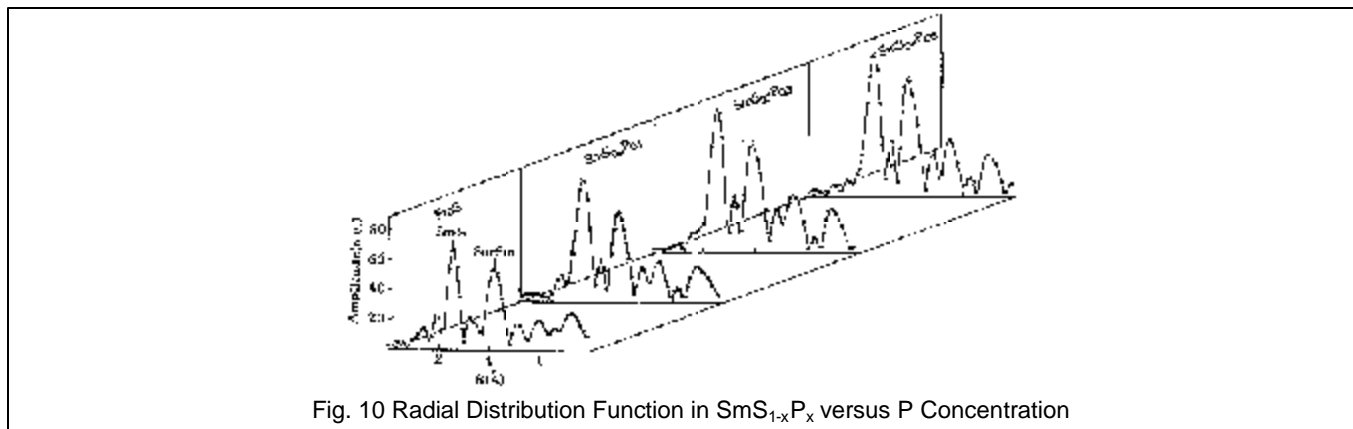


Fig. 10 Radial Distribution Function in $SmS_{1-x}P_x$ versus P Concentration

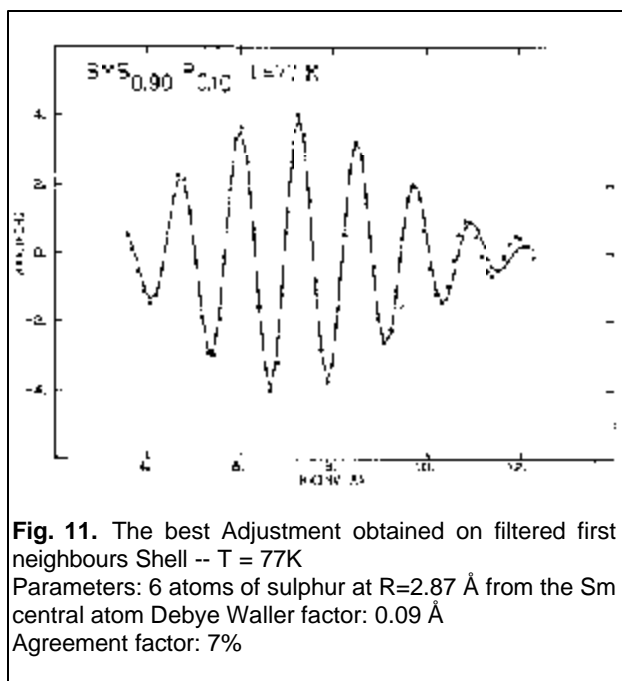


Fig. 11. The best Adjustment obtained on filtered first neighbours Shell -- T = 77K
Parameters: 6 atoms of sulphur at R=2.87 Å from the Sm central atom Debye Waller factor: 0.09 Å
Agreement factor: 7%

that the atomic relaxation is very small (less than 5.10^{-2} Å). Similar conclusion has been deduced from synchrotron radiation studies performed on other mixed-valent systems [8]. Nevertheless, the counting times remain rather long (1 to 10 hours) on the in-lab. spectrometer because of the rather low photon flux as compared to synchrotron radiation.

IV. Conclusion

The conclusions of our absorption investigations on an in-lab. X-Ray spectrometer is that reliable informations can be obtained:

1) *For near edge studies*, rather long counting times are necessary. Nevertheless, because the resolution is as good as for synchrotron experiments, and the access much easier, most of edge investigations can be performed at lab.;

2) *For Exafs studies*, the statistic remains insufficient to allow rigorous conclusions on physical problems, specially for dilute species. Nevertheless, it is very interesting for time-winning considerations to perform preliminary experiments at lab. before doing more precise experiments with synchrotron radiation.

In all cases, when we have to study low energy edges, it is absolutely necessary to run the rotating anode at low voltage in order to avoid high order harmonics.

References

1. a) G. Krill, J. P. Kappler, M. F. Ravet, C. Godart, J. P. Sénateur, Proc. ICVF (Köln, 1984), to be published in J. Mag. Mat.
b) J. Röhler, *ibid.* 1.a).
2. E. Beaupaire, G. Krill, J. P. Kappler and J. Röhler, Solid State Comm. **49**, n° 1 (1981) 65-69.
3. G. S. Knapp and P. Georgopoulos, in "Laboratories Exafs Facilities", ed. by E. A. Stern (American Institute of Physics, 1980) p. 2.
4. A. Jayaraman, P. Dernier and L. D. Longinotti, Phys. Rev. B Vol. 11, n° 8 (1975) 2783-94.
5. R. M. Martin, J. B. Boyce, J. W. Allen and F. Holtzberg, Phys. Rev. Lett. **44** (1980) 1275.
6. P. A. Lee, P. H. Citriti, P. Eisenberger and B. M. Kincaid. Rev. of Modern Physics **53**, n°4 Part 1 (1981) 769 804.
7. *Ibid.* ref. 6.
8. a) *Ibid.* ref. 1.
b) H. Launois, M. Rawiso, E. Holland-Moritz, R. Pott and D. Wohlleben, Phys. Rev. Lett. **44** (1980) 1271.
c) G. Krill, J. P. Kappler, J. Röhler, M. F. Ravet, J. M. Léger and F. Gautier, in "Valence Instabilities", ed. by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982) p. 155.