FLUORESCENCE DETECTION OF EXAFS:
SENSITIVITY ENHANCEMENT FOR DILUTE SPECIES AND THIN FILMS

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The fluorescence intensity is used to measure the X-ray absorption cross-section and is found to yield essentially the same results as a more conventional transmission experiment. However, the fluorescence method is shown to extend the sensitivity of the EXAFS technique by two or more orders of magnitude, and thus make feasible the study of extremely dilute species.

$$\Delta \mu_x = \frac{e}{2} \mu_t \left(\frac{1}{I_o} \right)^{\frac{1}{2}} \quad — ?$$

THE RECENT availability of broadband synchrotron radiation from electron storage rings has revived interest in the study of the extended X-ray absorption fine structure (EXAFS) [1]. Recent theoretical [2, 3] and experimental [4, 5] work has demonstrated the usefulness of the technique for studying the microstructural environment of the elements under study. Specifically one can determine the distance between a specific absorbing atom and its neighboring atoms, the choice of the absorbing atom being determined by the incident photon energy. To date, the experimental data in condensed materials have been limited to fairly concentrated species, because of the inherent limitations of the direct absorption technique. In this paper we wish to discuss a new method for measuring the X-ray absorption cross-section, which extends the sensitivity of the EXAFS technique by two or more orders of magnitude, and which therefore makes feasible the study of dilute systems, thin films, and surfaces. We shall make a quantitative comparison of this method with the direct absorption technique, show that the two techniques give essentially the same information, and then present data from a number of systems which would have been impossible to study by conventional means.

The direct absorption technique consists of measuring the incident and transmitted X-ray flux, I_0 and I respectively, and computing the absorption coefficient from the formula $\mu_t^d = \ln (I_0/I)$. In most cases the statistical precision of such a measurement is limited by the measurement of I; in this case the optimum sample thickness is $d = 2/\mu_t$, and the fractional statistical uncertainty is

i.e. 2 absorption length.

$$\Delta \mu_x / \mu_x = (e/2)(\mu_t/\mu_x)(1/I_0)^{1/2} \tag{1}$$

where μ_x, μ_b, and μ_t are the absorption coefficients for the species x, the background, and the total absorption coefficient, respectively, and which satisfy the following relations:

$$\mu_t = \mu_x + \mu_b$$
$$\mu_x = \sigma_x n_x. \tag{2}$$

The new technique makes use of the fact that an inner shell vacancy may relax by undergoing a radiative transition from a higher energy, occupied shell. The radiative probability ϵ, or "fluorescent yield", is a monotonically increasing function of atomic number, ranging from 0.30 for iron ($Z = 26$) to 0.75 for molybdenum ($Z = 42$). The fluorescence yield is expected to be independent of excitation energy for above threshold but may vary slightly near threshold. Thus the fluorescence intensity is a direct measure of the K-shell absorption probability, which is the single absorption mechanism of interest in EXAFS. This was checked experimentally as will be discussed shortly.

For simplicity we shall study the geometrical arrangement where the incident and fluorescent radiation make equal angles with the sample normal. The incident radiation has energy E, the fluorescent radiation has energy E_f, and the detector subtends a solid angle Ω. The fluorescence counting rate is then given by

$$I_f = I_0 \frac{\epsilon (\Omega/4\pi) \mu_x(E)}{\mu_t(E) + \mu_t(E_f)} \{1 - \exp[\mu_t(E) + \mu_t(E_f)] d\}. \tag{3}$$

Two important cases may now be distinguished: a thin,

Fluorescence yield Table p.9 (?) by Bertin

$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} \cdots$, for thin, conc case, only x survives, here,

concentrated sample, for which $[\mu_t(E) + \mu_t(E_f)]d \ll 1$, and a dilute, thick sample, for which $[\mu_t(E) + \mu_t(E_f)]d \gg 1$. In these two limits we have

$$I_f = I_0\epsilon(\Omega/4\pi)\mu_x(E)d \quad \text{(thin, concentrated)}$$

$$I_f = \frac{I_0\epsilon(\Omega/4\pi)\mu_x(E)}{\mu_t(E) + \mu_t(E_f)} \quad \text{(thick, dilute).} \quad (4)$$

The statistical precision is then given by

$$\frac{1}{I_f} \quad \Delta\mu_x/\mu_x = [I_0\epsilon(\Omega/4\pi)\mu_x(E)d]^{-1/2} \text{ (thin, concentrated)}$$

$$\Delta\mu_x/\mu_x = \left[\frac{\mu_t(E) + \mu_t(E_f)}{I_0\epsilon(\Omega/4\pi)\mu_x(E)}\right]^{1/2} \quad \text{(thick, dilute).} \quad (5)$$

Comparing equation (1) with equation (5), we see that the uncertainty of a transmission experiment scales as $1/\mu_x$, but for the fluorescence experiment the uncertainty scales as $(1/\mu_x)^{1/2}$. For dilute, thick samples we may set $\mu_t(E) = \mu_t(E_f)$, and the two techniques have equal sensitivity when $\mu_x = \epsilon(e^2/8)(\Omega/4\pi)\mu_t$. As a concrete example, we consider a dilute, aqueous solution of iron, assuming $\Omega/4\pi = 0.01$, $\mu_t = 14\,\text{cm}^{-1}$, and $\sigma_x = 3.85 \times 10^{-20}\,\text{cm}^2$, which yields $n_x = 1.0 \times 10^{18}\,\text{cm}^{-3}$. One can easily imagine a twentyfold or more improvement in detector solid angle, thus making the fluorescence technique competitive at concentrations as high as $2 \times 10^{19}\,\text{cm}^{-3}$.

The above arguments concern themselves only with the limitations imposed by the counting statistics. For the fluorescence experiments that we have performed, the precision is indeed statistics limited. However, for the transmission method, several systematic instrumental effects may distort the data and thus raise the lower limit on the concentration which is best studied by the fluorescence technique. Two such effects are sample inhomogeneity and fluctuating ratio of harmonic to fundamental intensity in the primary photon beam. When one measures a small signal in the presence of a large slowly varying background, very small instrumentally derived fluctuations in the background cannot be distinguished from the signal, and thus the apparatus must have a very high absolute stability. These problems are avoided by measuring the signal directly, as is the case with the fluorescence technique.

We have performed fluorescence measurements on a number of biological materials and solids, which clearly would have been impossible to perform by a direct absorption measurement. The fluorescence radiation was measured in all cases by a lithium-drifted germanium detector with an energy resolution of 200 eV (FWHM) and subtending a solid angle $\Omega/4\pi = 4.3 \times 10^{-4}$. The need for energy resolution becomes very important in dilute species because of the presence of a large elastically scattered component at the incident energy and a smaller inelastic Compton component. The germanium detector

can differentiate between those signals and the K_α fluorescence which occurs at energies lower than the edge energy. The energy differences among the three components will vary with the atom studied. With increased dilution the problem of detecting just the K_α fluorescence will become more severe and faster high resolution detectors will have to be developed. Atomic dilutions of the order of 10^{-5} to 10^{-6} can be studied with existing technology. The incident radiation monitor, monochrometer, and control hardware were identical to those used in transmission experiments described elsewhere [1].
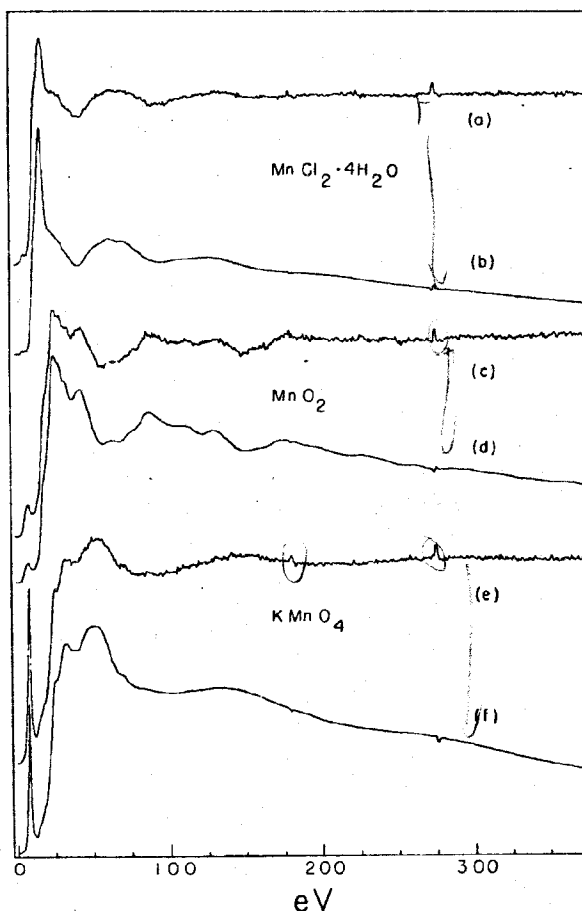

Fig. 1. Comparison of fluorescence detection (a, c, e) with normal transmission studies (b, d, f) of the EXAFS structure of concentrated Mn in three different systems.

To verify the assumption that the information accessible via the absorption and fluorescent experiments are the same, we performed comparative experiments on a variety of samples for a number of elements including Fe, Mn, Mo, Pb, Zn, Cu and Co. Representative data are shown in Fig. 1 where are plotted absorption and
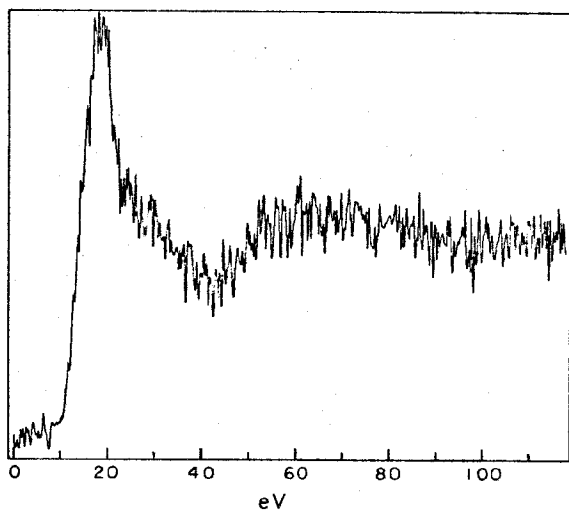
Jablevic et al. Solid State Comm. 23, 679 (1977).

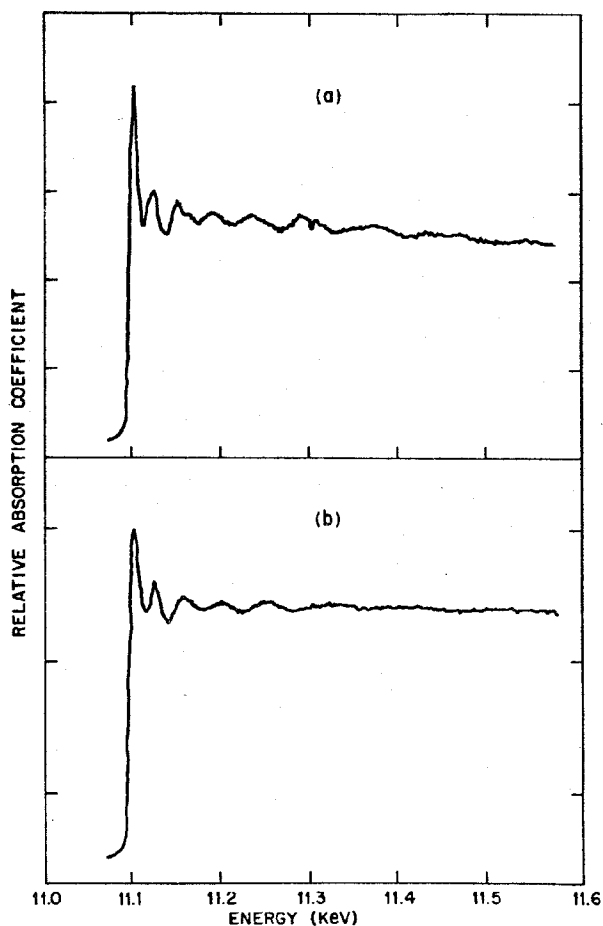Fig. 2. The absorption spectrum of Mn in a leaf taken by fluorescence detection.

Fig. 3. Study of the absorption spectrum of two Nb_3Ge films by fluorescence detection. The films are characterized by (a) $T_d = 921$ K, $T_c = 21$ K, (b) $T_d = 800$ K, $T_c = 5$ K.
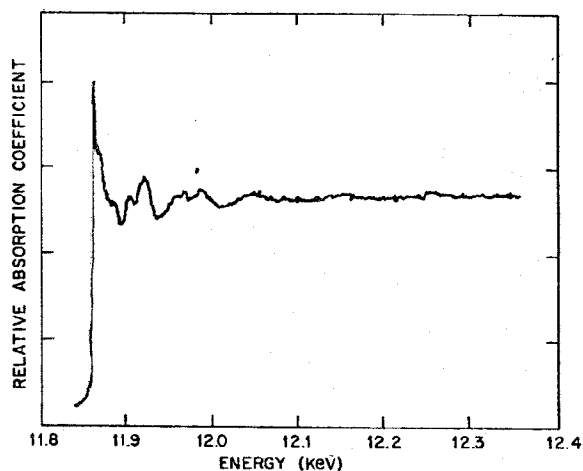

Fig. 4. The fluorescence detector absorption spectrum of arsenic in silicon.

fluorescence spectra for three manganese compounds of different formal oxidation state and crystal structure. For each pair of spectra it is seen that the curves are essentially identical although there are some slight differences in relative intensities below threshold region. These are probably a result of the energy dependence of the fluorescence yield. The EXAFS features are virtually identical.

The sensitivity of the fluorescence method is amply demonstrated in Fig. 2 where we have plotted the spectrum of the Mn in a leaf. The concentration of Mn in the chloroplasts of green plants is $ca.$ 10–50 ppm and this element is essential for oxygen evolution. This spectrum required hours of signal averaging to achieve. Comparable times were devoted to absorption experiments with negative results.

Figure 3 shows the EXAFS spectra for the Ge edge of two Nb_3Ge films sputtered onto sapphire substrates at different deposition temperatures T_d. Although the two samples differ markedly in superconducting transition temperatures T_c, X-ray diffraction analysis reveals that both films consist principally of the A15 phase, with lattice parameter $a = 5.13 \pm 0.01$ Å. Preliminary analysis of the EXAFS spectra indicates that the low T_c films has Ge–Nb distance characteristic of low T_c, bulk crystals (2.87 Å), but that the high T_c films has a much larger Nb–Ge distance, 3.2 Å. This is easily seen from Fig. 3. The larger distance corresponds to more rapid wiggles [2, 3] of the EXAFS pattern. These samples, falling within the "thin, concentrated" limit of the previous analysis, could not have been studied by the direct absorption technique.

Figure 4 shows the EXAFS spectrum for the As edge of a single Si crystal doped with As at a concentration $n = 2–4 \times 10^{19}$ cm^{-3}. From these data we hope to extract information about the location of the As atom

in the host crystal, and perhaps information about the distortion of the lattice immediately surrounding the heavy impurity.

It was shown that one can obtain the same information by fluorescence detection as by transmission measurements. The fluorescence measurement has inherent advantages for dilute species which were demonstrated by the leaf and thin film results. There are a large number of exciting areas of this new technique and towards this end we are already constructing a multidetector fluorescence system capable of collection over a larger solid angle. This should improve the statistical quality of our measurements or alternatively extend the range of dilution that can be studied.

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