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# Fluorescence Detection of Extended X-Ray Absorption Fine Structure in Thin Films

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**Abstract.** — The linearity of the fluorescence detection of the Extended X-ray Absorption Fine Structure (EXAFS) signal of moderately thin film samples depends on the experiment geometry and on the sample thickness because of the self-absorption effect. The correction for thick samples has been extensively studied but there has not been reported a method which could be useable continuously for intermediate thickness. We propose an approximative method that, taking into account the sample thickness, will provide the correction of the EXAFS signal amplitude. In the present work, the correction is applied to two different systems: FeSi<sub>2</sub> thin films and Co/Cu superlattices. After correction, the determination of the crystallographic phase of FeSi<sub>2</sub> thin films over different substrates has been carried out.

## 1. Introduction

The study of structural properties of thin films using X-ray Absorption Spectroscopy (XAS) has received an increased attention in the last few years [1]. This technique presents some advantages compared to the X-ray diffraction. XAS is an element-specific probe of the local environment of the absorbing atom. By tuning the incoming X-ray energy, one obtains the fine structure at and above the absorption edge of the selected atom. The structural information contained in this spectrum is as follows: i) the pre-edge structure is related to the site symmetry and valence state; ii) the X-ray Absorption Near Edge Structure (XANES) region contains stereo chemical information (*e.g.* bond angles); and iii) the Extended X-ray Absorption Fine Structure (EXAFS) oscillations give accurate atomic distances and coordination numbers from the absorber to its neighbors. For example in superlattices, the advantage respect to X-ray diffraction is that, while diffraction yields information on the average structure of the two components modulated by the superlattice periodicity, EXAFS enables to select one of them eliminating the long-range periodicities.

Fluorescence yield detection is a good method to measure the EXAFS signal because it is very sensitive for samples with small quantity of matter [2,3] and because the probing depth

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is large enough to be sure that the bulk structure is sounded. When the sample is not thin enough, the fluorescence detected EXAFS signal is not proportional to the actual oscillation of the absorption coefficient, and must be corrected because of the self-absorption effect. A high concentration of the absorbing atoms makes possible the re-absorption of their own fluorescence yield and the obtained EXAFS signal becomes smaller than the actual one. Typically, this effect is found in samples with big amount of absorbing atoms: non-diluted samples and non-thin films. An important magnitude is the information depth, *i.e.* the thickness of the sample, beginning from the surface, where the detected fluorescence yield is mainly emitted. The information depth changes with the geometry of the experiment: it becomes maximum when the surface of the sample forms an angle near  $45^\circ$  with the incoming beam and with the fluorescence detector, at this position the absorption of the incident X-ray and the emitted fluorescence yield are of the same order and the sounded depth results maximum.

Self-absorption effect has been studied by Goulon [4]. For thick enough samples, the relationship between the fluorescence experimental EXAFS signal,  $\chi_{\text{exp}}(k)$ , and the actual value  $\chi(k)$  has been reported by Troeger *et al.* [5]. Nevertheless, an interesting point is to know where is the boundary between thin samples and thick ones.

In this work, we propose a new approximation in order to correct the self-absorption effect in samples of arbitrary thickness, where the correction factor is calculated from the actual film thickness and from the information depth for this material. The correction is specially interesting for middle range thickness films ( $100 \text{ \AA} < d < 10,000 \text{ \AA}$ ). It will be tested in two different systems: FeSi<sub>2</sub> thin films and Co/Cu superlattices prepared over Si and Cu(100) single crystals, respectively.

## 2. X-Ray Absorption Spectroscopy in Moderate Thin Films

When some element environment (for example Fe) is studied inside a compound by fluorescence detected EXAFS spectroscopy, the fluorescence counting rate is given by [5]

$$\frac{I(E)}{I_0(E)} = \frac{A}{r^2} \varepsilon_{\text{Fe}} \frac{\mu_{\text{Fe}}(E)}{\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_f) \sin(\phi)/\sin(\theta)} \left[ 1 - \exp \left( - \left( \frac{\mu_{\text{tot}}(E)}{\sin(\phi)} + \frac{\mu_{\text{tot}}(E_f)}{\sin(\theta)} \right) d \right) \right]. \quad (1)$$

This expression has been derived for the averaged intensity of the fluorescence  $I(E)$  relative to the incidence intensity  $I_0(E)$ ,  $A/r^2$  is the solid angle from the sample to the detector,  $\varepsilon_{\text{Fe}}$  is the iron fluorescence yield,  $\mu_{\text{Fe}}$  is the absorption due to iron and  $\mu_{\text{tot}}$  is the total absorption coefficient due to all the elements present in the sample,  $d$  is the thickness of the sample,  $E_f$  is the emission fluorescence energy of the iron and  $\phi$  is the X-ray incidence angle over the sample and  $\theta$  is the angle between the sample and the detector (in our experimental set-up  $\phi = 90 - \theta$  and  $g = \tan \phi$ ). Figure 1 is a schematic representation of the geometry for fluorescence detection.

For very thin samples the relation  $[\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_f)g]d \ll 1$  is satisfied. Then, expanding the exponential term in equation (1), the fluorescence yield is proportional to  $\mu_{\text{Fe}}(E)$ . This means that no correction is needed to evaluate the EXAFS signal.

On the other hand, for thick samples:  $[\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_f)g]d \gg 1$ , then the fluorescence yield is proportional to  $I_0 \mu_{\text{Fe}}(E)/[\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_f)g]$ . After Troeger *et al.* [5], the corresponding correction can be easily carried out. The experimentally obtained EXAFS oscillations ( $\chi_{\text{exp}}(E)$ ) must be corrected to obtain the actual signal ( $\chi_{\text{Fe}}(E)$ ), by

$$\chi_{\text{exp}}(E) = \chi_{\text{Fe}}(E) \left[ 1 - \frac{\bar{\mu}_{\text{Fe}}(E)}{\bar{\mu}_{\text{tot}}(E) + \bar{\mu}_{\text{tot}}(E_f)g} \right] = \chi_{\text{Fe}}(E)[1 - S(E)]. \quad (2)$$

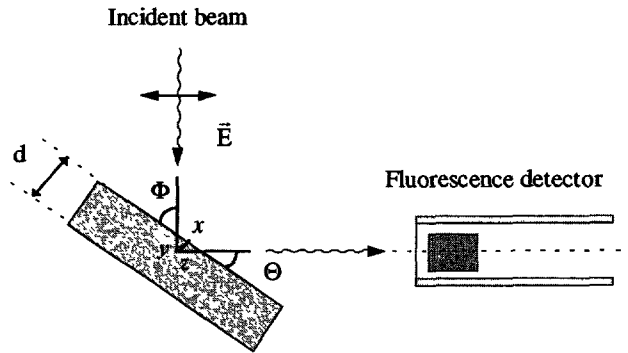


Fig. 1. — Experimental geometry for fluorescence yield detection.

It must be noted that here the total absorption and the iron (central element) absorption have been written as  $\bar{\mu}_{\text{tot}}$  and  $\bar{\mu}_{\text{Fe}}$ , respectively, because they refer to the atomic absorption coefficients.

Thin films, with thickness ranging from some hundred to some thousands angstroms, usually give an intermediate situation:  $[\bar{\mu}(E) + \bar{\mu}_{\text{tot}}(E_f)g]d \leq 1$ . In this case, the point to be considered is the concentration of the absorbing element into the sounded sample. But now the relevant value of concentration for the absorbing element is its content in a thickness equal to the information depth. The reason to take this thickness is that the contribution to  $\mu_{\text{tot}}$  comes from the film and also from the substrate and the information depth for the film seems a good approximation to the actual value. So, it is necessary to evaluate the information depth in order to know if, for such a thickness, the content of the absorbing element allows to consider the sample diluted enough to have a good linearity between the fluorescence measurement and the actual EXAFS signal.

The information depth ( $\lambda_f$ ) of the fluorescence yield detection has been defined in reference [5] as the expectation value of the depth perpendicular to the surface in which the detected fluorescence photons are generated. It results to be given by the following expression:

$$\lambda_f = \frac{\sin \phi}{\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_f)g} \quad (3)$$

In our calculations of  $\lambda_f$  instead  $\mu_{\text{tot}}$ , we have used the atomic coefficients,  $\bar{\mu}_{\text{tot}}$ , which are the only accessible in the X-ray cross section tables.

Generally, for the middle range thickness the concentration of the absorbing element into the information depth does not satisfies  $\bar{\mu}_{\text{Fe}}/\bar{\mu}_{\text{tot}} \leq 0.1$  which, after Tan *et al.* [6], would be the criterium to consider a sample as sufficiently diluted from the point of view of the X-ray absorption spectroscopy. Thus, under these conditions, the actual case is a concentrated sample for which we know how to correct the signal.

In summary, we propose the method so-called "Ideal dilution of the thin film into a determined substrate thickness". To correct the experimental EXAFS signal, it can be described by the following procedure: i) to evaluate the information depth for the film material (it must be evaluated for the experimental angle of incidence); ii) to calculate the concentration of the absorbing atom into a virtual material obtained from the dilution of the film thickness into a substrate thickness equal to the information depth minus the film thickness, on this way,

the total thickness of the virtual material will be equal to the information depth; and iii) to correct the experimental EXAFS signal as it was coming from this virtual material by using equation (2).

On this way, both limits are recovered: for thickness much more smaller than the information depth, this dilution approximation implies the "non correction" as it can be seen in equation (2) where  $S(E)$  is almost zero for very small concentrations of the absorbing atom. On the other hand, when the film thickness is bigger than the information depth, it is the correction given by Troeger *et al.* which is valid, this situation being reached for thick film samples and for glancing angles.

### 3. Experimental

The following Extended X-ray Absorption Fine Structure (EXAFS) experiments were carried out at the XAS-3 beamline at DCI storage ring (Orsay) with an electron beam energy of 1.85 GeV and an average current of 250 mA. Data were collected by using a fixed exit monochromator with two flat Si(311) crystals, detection was made by using one ion chamber with air fill gas and a photomultiplier tube with a scintillator plastic in order to detect the fluorescence yield [7] at the Fe and Co K-edges in FeSi<sub>2</sub> thin films and Co/Cu superlattices, respectively. Several spectra were collected in order to accumulate them and to have a good enough signal to noise ratio. Energy resolution was estimated to be about 2 eV by the Cu foil 3d near edge feature. The energy calibration was monitored using the Cu foil sample, and was taken as 8991 eV at the first maximum above the edge.

Fluorescence spectra were obtained at room temperature with a geometry where the fluorescence detector forms an angle of 90° with the incoming beam. The Bragg diffraction peaks of the crystalline substrates were avoided by looking for a proper angle between the sample and the detector.

### 4. Results and Discussion

We have performed experiments in two different systems in order to test the proposed method: the first one is related to the determination of the crystallographic phase of iron silicide films over some Si substrates and the second one studies the influence of the self-absorption effect on the determination of the structural properties of the Co layers in Co/Cu superlattices.

**4.1. IRON SILICIDE THIN FILMS.** — The iron fluorescence EXAFS spectra obtained from several samples are shown in Figure 2. Two iron silicide thin films samples grown over Si(100) and Si(111) substrates (with thickness 500 and 1500 Å, respectively) have been studied and compared with two reference compounds:  $\alpha$ -FeSi<sub>2</sub> single crystal and CoSi<sub>2</sub> (fluorite type structure).

The expression  $[\bar{\mu}_{\text{tot}}(E) + \bar{\mu}_{\text{tot}}(E_f)g]d$  for these thin films, gives values in the 0.01–0.03 range. In principle, it could be considered small enough to be negligible. Nevertheless, the evaluation of the  $\bar{\mu}_{\text{Fe}}/\bar{\mu}_{\text{tot}}$  gives values in the 0.1–0.3 range which according to reference [6], shows that these samples can not be considered as diluted ones. Moreover, the dependence of the amplitude oscillations with the incidence angle shows that the EXAFS signal is affected by the self-absorption effect, the experimental EXAFS intensity being not proportional to the actual EXAFS signal. Indeed, the expression  $[\bar{\mu}_{\text{tot}}(E) + \bar{\mu}_{\text{tot}}(E_f)g]d$  increases when the incidence angle decreases becoming near 1 for glancing angles. Therefore, it is necessary to find the correction for the measured signal that, taking into account the film thickness and the

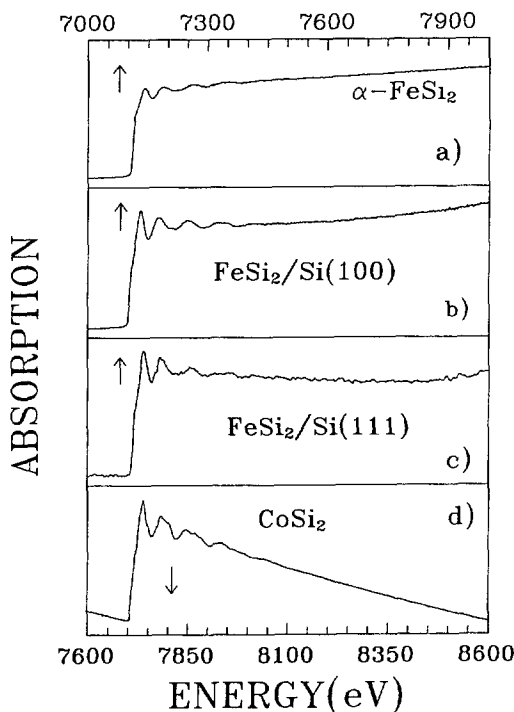


Fig 2. — Fluorescence absorption spectra at the Fe K-edge of several samples: a)  $\alpha$ -FeSi<sub>2</sub> single crystal; b) FeSi<sub>2</sub> film over Si(100) (thickness 1500 Å), c) FeSi<sub>2</sub> film over Si(111) (thickness 500 Å); d) transmission absorption spectrum at the Co K-edge of polycrystalline CoSi<sub>2</sub> fluorite-type structure.

incidence angle, would be able to cover the range from one monolayer (where no correction is needed) to bulk samples (where the correction expression has been already determined).

We have calculated the information depth for a  $\alpha$ -FeSi<sub>2</sub> single crystal measured at some particular incidence angles, by using the expression of equation (3). Functions are shown in Figure 3a, a small difference can be observed for these two incidence angles. These functions show that the X-ray absorption and fluorescence emission processes occur at about 40,000 Å from the surface.

First of all, we have tried to explain properly the spectrum obtained from bulk  $\alpha$ -FeSi<sub>2</sub> single crystal which we have measured in fluorescence mode and that we want to use as a reference compound. By using equation (2), we have calculated the corresponding  $S(k)$  function showed in Figure 3b in order to correct the EXAFS signal. Figure 4a shows the change of EXAFS signal by the correction. Their Fourier transform magnitudes are also plotted in Figure 5a. After correction, it has been obtained a proper fit of the EXAFS parameters, as it can be seen at the appendix

In order to correct the EXAFS signal obtained from iron silicide films over Si, we have followed the proposed approximation: the EXAFS signal obtained from the film by fluorescence detection will be corrected by considering a "virtual" medium having a composition obtained by the dilution of the film compound into a substrate thickness equal to the information depth of the film compound. This is justified because the main decrease of the X-ray intensity after the absorption from a thin film happens at the beginning of the X-ray path inside the film.

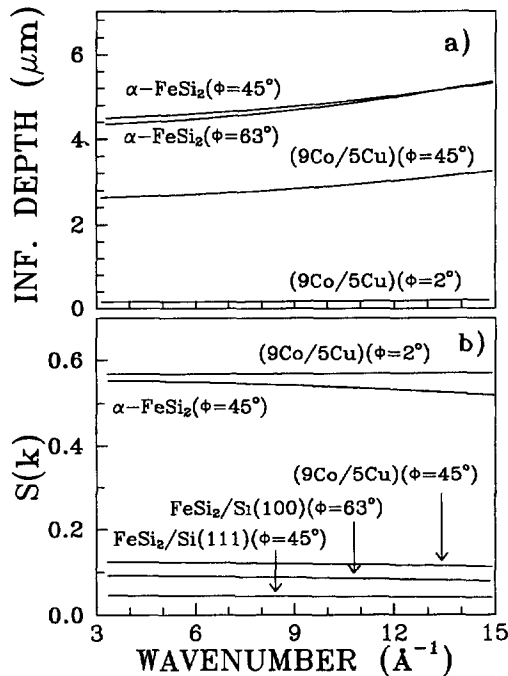


Fig. 3 — a) Information depth for  $\alpha\text{-FeSi}_2$  single crystals and 9Co/5Cu superlattices at some X-ray incidence angles at the Fe and Co K-edges, respectively. b) Self-absorption correction factor  $S(k)$  for  $\alpha\text{-FeSi}_2$  bulk,  $\text{FeSi}_2$  thin films and Co/Cu superlattice, evaluated at several X-ray incidence angles.

Information depth functions are plotted in Figure 3a for the two experimental angles. Following the approximation, the self-absorption term  $S(E)$ , corresponding to the two measured samples, has been calculated and it has been plotted in Figure 3b. It has been plotted the  $S(E)$  function as  $S(k)$  depending on the wavenumber  $k = (E/2m_e)^{1/2}$ . We will distinguish the two  $\text{FeSi}_2$  films as prepared over Si(100) or over Si(111), the thickness of which was 500 Å and 1500 Å, respectively. For  $\text{FeSi}_2$  films, the  $S(k)$  function has been evaluated for a virtual compound of Fe and Si with a Fe concentration calculated by taking into account the Fe amount of the film diluted in a volume of substrate (Si) given by a thickness equal to the information probing depth of the  $\text{FeSi}_2$ . The difference in  $S(k)$  factor, plotted in Figure 3b, is mainly due to the different concentrations of Fe in the  $\alpha\text{-FeSi}_2$  single crystal and the obtained values for the virtual compound related to the 500 and 1500 Å films over Si(111) and Si(100), respectively.

This correction has been applied to the experimental EXAFS signals following the expression:  $\chi_{\text{exp}}(k) = \chi_{\text{Fe}}(k)(1 - S(k))$ . In order to have a picture of how big the correction is,  $\chi_{\text{exp}}(k)$  and  $\chi_{\text{Fe}}(k)$  have been plotted in Figure 4 (and their Fourier transform magnitudes in Fig. 5) for all the samples. It has been also plotted  $\chi_{\text{Co}}(k)$  for the transmission measurements of  $\text{CoSi}_2$ .  $\text{CoSi}_2$  can be used as a reference compound due to similarity between cobalt and iron and because distances and coordination numbers are similar in both silicides. From this plot, after correction, the Fe and Co signals are now comparable but a quantitative analysis will be performed in order to determine the crystallographic phase of the thin films. The complete EXAFS analysis is presented in the Appendix.

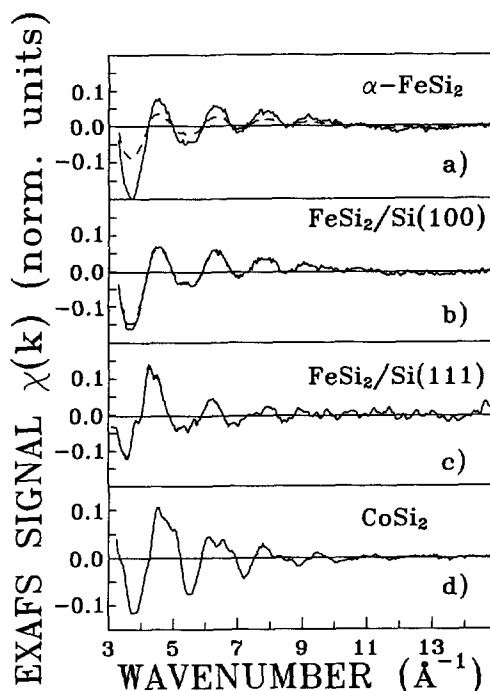


Fig. 4. — Normalized EXAFS signal from Figure 2 data, after atomic background subtraction by a cubic spline polynome. a), b) and c) Dashed lines are the non-corrected EXAFS signal and continuous lines are EXAFS spectra after correction; d) this spectrum has been detected by the transmission mode and no correction is needed

4.2. Co/Cu SUPERLATTICES. — Similarly to the previous system, cobalt fluorescence EXAFS spectra has been performed for the  $(9\text{Co}/5\text{Cu})_{103}$  single crystal superlattice prepared over Cu(100) at several incident angles (the notation means that the bilayers are formed by 9 and 5 atomic layers of Co and Cu, respectively, and this bilayer is repeated 103 times). In Figure 3 are also showed the penetration depth and the self-absorption factor for two characteristic angles  $\phi = 45^\circ$  and glancing  $\phi = 2^\circ$ . The Fourier transform  $k^3\chi(k)$  obtained for the spectra performed at this two geometries are plotted in Figure 6. We have followed the same method in order to correct the fluorescence EXAFS signal. For the  $\phi = 45^\circ$  spectra the correction has been calculated for a virtual sample where the cobalt of the superlattice has been diluted in 28,000 Å of copper. Nevertheless, the signal information depth for glancing angle result to be approximately 1,600 Å which is smaller than the total thickness of the superlattice (2,700 Å) So, the correction to be performed is the same as for an infinitely thick  $(9\text{Co}/5\text{Cu})$  compound. The Fourier transform before and after correction has been also plotted in Figure 6. It has been calculated following the EXAFS standard and criteria to obtain the magnitude in  $\text{Å}^{-4}$  units.

It is clear that the first four distances can be observed at 2.3, 3.5, 4.2 and 4.8 Å showing a fcc structure for the cobalt layers which is imposed by the copper ones. In order to perform polarization dependent EXAFS experiments it is necessary to change the incident angle and the signal must be corrected to analyze data in a proper way. The apparent decrease of the experimental signal cannot be related to structural or polarization dependent features as it



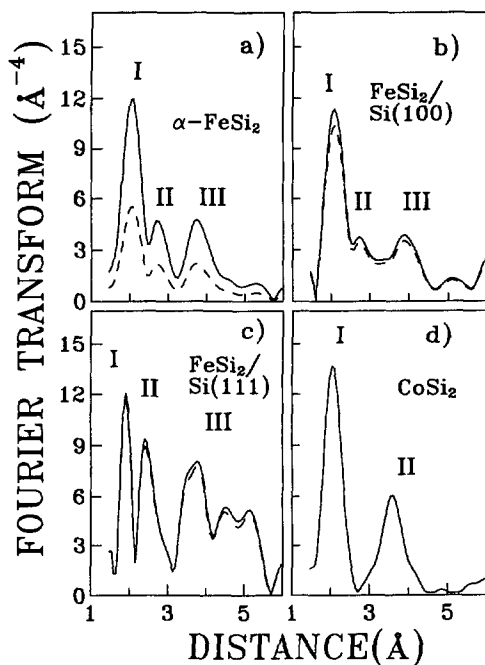


Fig. 5. — Fourier transform magnitude of EXAFS signals from Figure 4 spectra. In order to observe the effect of the self-absorption correction in the fluorescence detected spectra (a), (b) and (c), dashed lines corresponds to the non-corrected EXAFS signal and continuous lines are the Fourier transform of the self-absorption corrected data.

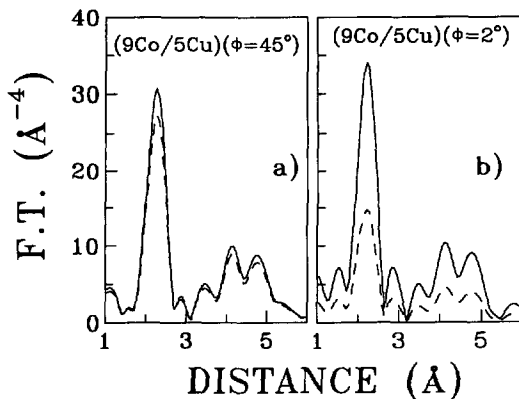


Fig. 6. — Fourier transform magnitudes of  $(9\text{Co}/5\text{Cu})_{103}$  superlattice before and after self-absorption correction (dashed and continuous lines, respectively) from the spectra performed at two different geometries: a) X-ray sample incidence angle  $\phi = 45^\circ$ , b)  $\phi = 2^\circ$

could be done by a first look. After self-absorption correction the magnitude of the EXAFS signal is not affected by the incident angle and only a very small shift is observed which after a careful analysis has been related to a new tetragonally distorted crystallographic phase of Co layers [8]. A more detailed analysis of the polarization dependent EXAFS experiments has been performed elsewhere [8] and it has been shown that the actual Co layers structure is face centered tetragonal, where the base plane (parallel to the layers) is imposed by the copper lattice constant and the  $c$ -axis is contracted in such a way that the atomic volume of the thermodynamical stable Co hexagonal phase was conserved.

## Conclusions

We propose a new method to correct the EXAFS signal obtained by fluorescence detection of moderately thick films (typically for thickness between 100 Å and 10,000 Å) which is erroneous because of self-absorption effects. The method can be described as consisting in a "ideal dilution" of the film into a substrate thickness equal to the information depth of the film compound

The method has been tested in FeSi<sub>2</sub> films and, thanks to the correction, it has been possible to identify the  $\alpha$ - and  $\beta$ -crystallographic phases in FeSi<sub>2</sub>/Si(100) and FeSi<sub>2</sub>/Si(111) film, respectively. On the other hand, it has been applied to Co/Cu superlattices in order to make possible studies with different incident angles, for example polarization dependent EXAFS spectroscopy shows a tetragonally distorted crystallographic phase of Co layers.

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## Appendix: Analysis of Exafs Data

The FeSi<sub>2</sub> EXAFS data have been analyzed in a standard way. The pseudo-radial distribution function is obtained weighting the EXAFS signal  $\chi(k)$  by the cubic wavenumber ( $k^3$ ), multiplying by a Hanning window within the interval from 3.0 to 14.0 Å<sup>-1</sup> and Fourier transforming. The Fourier transform magnitudes are shown in Figure 5; they have been calculated following the convention given at the Standard and Criteria Report [9], their units are Å<sup>-4</sup> for comparison purposes. After the correction, it can be observed that the RDF is similar in magnitude to the obtained from the fluorite CoSi<sub>2</sub> structure which has been measured by the transmission method and to the  $\alpha$ -FeSi<sub>2</sub> single crystal where clearly the correction must be applied.

Table I. — *Crystallographic distances and coordination numbers of  $\alpha$ -FeSi<sub>2</sub>,  $\beta$ -FeSi<sub>2</sub> and CoSi<sub>2</sub> (fluorite structure).  $\sigma_j$  is the fitted Debye-Waller factor, and  $\epsilon$  is the deviation of the calculated signal from the experimental data, defined as  $\epsilon^2 = (1/n)\Sigma(\text{data}_i - \text{model}_i)^2$ . In the fitting processes the coordination number and the distances have been fixed to the crystallographic values and it has been performed by using the backscattering phases and amplitudes reported by Rehr *et al.* in reference [11].*

sample	pair	$N$	$d$ (Å)	peak	$\sigma$ (Å <sup>2</sup> )	$\epsilon$
$\alpha$ -FeSi <sub>2</sub>	Fe-Si	8	2.350	I & II	0.074	$2.7 \times 10^{-5}$
	Fe-Fe	4	2.684		0.092	
	Fe-Fe	4	3.795	III	0.068	$1.2 \times 10^{-4}$
	Fe-Si	8	4.197		0.073	
$\beta$ -FeSi <sub>2</sub>	Fe-Si	4	2.335			
	Fe-Si	2	2.380			
	Fe-Si	2	2.433			
	Fe-Fe	2	2.967			
	Fe-Fe	4	3.971			
	Fe-Si	3	4.018			
	Fe-Fe	4	4.026			
	Fe-Fe	2	4.044			
	Fe-Si	1	4.055			
CoSi <sub>2</sub> fluorite	Co-Si	8	2.317	I	0.084	$3.1 \times 10^{-5}$
	Co-Co	12	3.803	II	0.105	$2.6 \times 10^{-5}$

In order to probe the validity of this correction, a quantitative evaluation of the results has been carried out by fitting the EXAFS oscillation to the well known expression [10]:

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} \exp(-2k^2\sigma_j^2) \exp(-\Gamma_j R_j/k) f_j(k) \sin[2kR_j + \Phi_j(k)]. \quad (4)$$

Equation (4) describes the EXAFS oscillations for a Gaussian distribution of  $N_j$  atoms at mean distances  $R_j$  around the absorbing atom considering single scattering and plane-wave approximation.  $\sigma_j$  is the Debye-Waller factor, and  $\phi_j(k) = 2\delta(k) + \gamma_j(k)$  is the phase shift,  $\delta(k)$  and  $\gamma_j(k)$  being the central and backscattering atom phase shifts, respectively.  $f_j(k)$  is the magnitude of the backscattering amplitude of the  $j^{\text{th}}$ -neighbor atom,  $k/\Gamma_j$  is a convolution of the mean free path of the photoelectron traveling from the absorbing atom to the backscatterer in the  $j^{\text{th}}$  shell and the lifetime of the core hole.

Table I gives the crystallographic distances of reference compounds considered in the determination of the structure of the FeSi<sub>2</sub> films. Due to the slightly different distance values of the coordination shells of the  $\beta$ -FeSi<sub>2</sub> phase, distances have been averaged when they differs less than 0.0189. Table I gives also the parameters and standard deviations for the best fit of the corrected EXAFS signals of  $\alpha$ -FeSi<sub>2</sub> single crystal showing to be similar in magnitude as the obtained for CoSi<sub>2</sub> (fluorite-type phase). Fitting calculations have been performed by using the backscattering phase and amplitude functions reported by Rehr *et al.* [11].

Table II. — EXAFS parameters of the self-absorption corrected signal after fitting procedures for different samples. Coordination numbers have been fixed to the crystallographic values.

sample	pair	peak	$N_j$	$R_j$ (Å)	$\sigma$ (Å <sup>2</sup> )	$\epsilon$
FeSi <sub>2</sub> / Si(100)	Fe-Si	I & II	8	2.35	0.074	$2.4 \times 10^{-5}$
	Fe-Fe		4	2.68	0.095	
	Fe-Fe	III	4	3.795	0.074	$9.0 \times 10^{-4}$
	Fe-Si		8	4.20	0.080	
FeSi <sub>2</sub> / Si(111)	Fe-Si	I	4	2.28	0.042	$4.5 \times 10^{-4}$
	Fe-Si		2	2.38	0.082	
	Fe-Si		2	2.43	0.054	
	Fe-Fe	II	2	2.80	0.001	$2.4 \times 10^{-4}$
	Fe-Fe		4	2.97	0.044	
	Fe-Si	III	3	4.02	0.025	$2.0 \times 10^{-4}$
	Fe-Fe		4	4.03	0.046	
	Fe-Fe		2	4.04	0.046	
	Fe-Si		1	4.05	0.025	

FeSi<sub>2</sub> thin film data have been compared to both  $\alpha$ - and  $\beta$ -crystallographic environments, Table II is the summary of the best fits. Fitting have been performed by using both theoretical function from reference [11] and experimental backscattering phases and amplitudes obtained from CoSi<sub>2</sub> (to simulate Fe-Si and Fe-Fe pairs). No substantial differences have been observed between both fits.

Figure 7 shows the  $k$ -space comparison between the experimental EXAFS filtered data and the calculated  $\chi(k)$  signal from equation (4). After Figure 7 comparisons and inspection of values in Table II, it is possible to conclude that the FeSi<sub>2</sub>/Si(100) (thickness 1500 Å) and FeSi<sub>2</sub>/Si(111) (thickness 500 Å) thin films have been crystallized under two different phases corresponding to the so-called  $\alpha$ - and  $\beta$ -FeSi<sub>2</sub> crystallographic structures, respectively. When the comparison procedure is performed by selecting for each sample the other crystallographic phase or even a fluorite-type phase, the  $R$ - and  $k$ -fits become impossible, showing that some other selection different from that given in Table II is not consistent with EXAFS experiments.

The results of the crystallographic characterization of these particular samples can not be generalized to other films grown over the same substrates because there are many parameters in the growing process that may change the properties of the iron disilicide film. In the present work, the structural characterization is given only to illustrate the correction method and, in principle, they are consistent with previous reported determination of the crystallographic phases by surface techniques [12].

It is important to remark that the self-absorption correction has been very important in order to fit properly the EXAFS signal. In complex structures as FeSi<sub>2</sub> phases, the coordination numbers and Debye-Waller factors are fully correlated with pair distances and the analysis of the distorted experimental data without self-absorption correction may provide erroneous conclusions in the determination of the actual crystallographic phase.

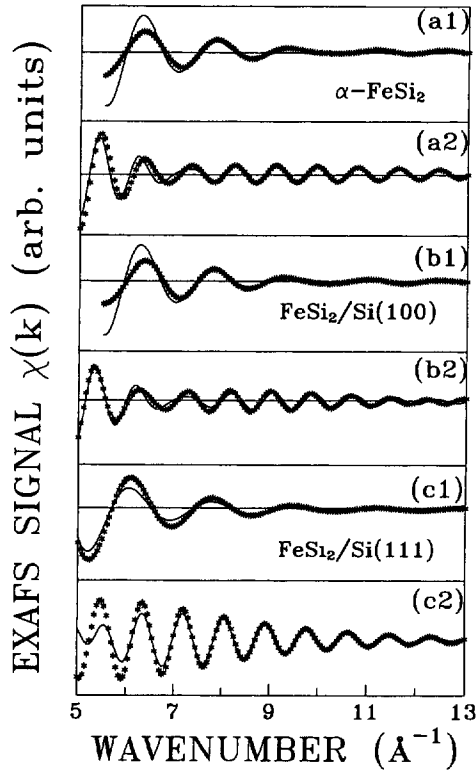


Fig. 7. —  $k$ -space comparison of calculated EXAFS signal (solid line) and experimental filtered data (discrete points): a)  $\alpha$ -FeSi<sub>2</sub> single crystal, (a1) I and II labeled (in Fig. 5) Fourier transform peaks from 1.47 to 3.13 Å; (a2) III peak from 3.313 to 4.357 Å. b) FeSi<sub>2</sub>/Si(100) thin film, (b1) I and II Fourier transform peaks from 1.595 to 3.129 Å, (b2) III peak 3.252 to 4.357 Å. c) FeSi<sub>2</sub>/Si(111) thin film, (c1) I Fourier transform peak from 1.657 to 2.148 Å, (c2) II Fourier peak from 2.209 to 2.823 Å.

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