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DOUBLE-ELECTRON EXCITATION AT THE Si K-EDGE OF AMORPHOUS SILICON

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ABSTRACT

In this paper we report the experimental evidence of a double-electron excitation involving two deep core states in the X-ray absorption coefficient of a solid amorphous system. For the first time a fine structure (EXAFS) in a double-electron excitation cross section has been identified. Such feature has unambiguously allowed us to assign the dominant excitation channel to a  $(1s,2p) \rightarrow (3p,\epsilon p)$  shake-up transition.

1. INTRODUCTION

Double electron excitations have been observed since the late sixties in pioneering works on the X-ray absorption coefficients of atoms as described by Fano and Cooper<sup>1</sup>.

Excitations involving two deep core states occur in the region of the EXAFS oscillation, therefore they have been easily identified either in orderless systems like noble gases<sup>2</sup> or in solids well after the edge in the energy region where the EXAFS signal is weak<sup>3</sup>.

Disordered systems like amorphous solids are a further candidate for the identification of multi-electron excitations. In the present work we report the results of a thorough investigation of the EXAFS region above the K-edge in hydrogenated amorphous silicon (*a*-Si:H). As usual for amorphous systems, the spectrum is dominated by a single frequency EXAFS signal coming from the first nearest neighbours. However, small but detectable distortions, arising from two different effects, are present. We already identified<sup>4</sup> a residual structural high frequency signal, mainly due to the second coordination shell, and a step like signal 124 eV above the K-edge, which was attributed to the opening of a two electron excitation channel. In the present work we investigate in more details this second feature.

2. EXPERIMENTAL

The *a*-Si:H sample was deposited by glow-discharge on a 12.5 $\mu$  thick Beryllium foil. The hydrogen content of the sample (14%) was measured by infrared spectroscopy integrating the Si-H wagging mode at 640  $cm^{-1}$ .

In order to obtain the experimental double excitation cross section with an appropriate signal to noise ratio, the sample was measured for 4 hours of dedicated beam time at LURE (Orsay) on the low energy storage ring ACO. The averaged spectrum resulted of very good quality with a

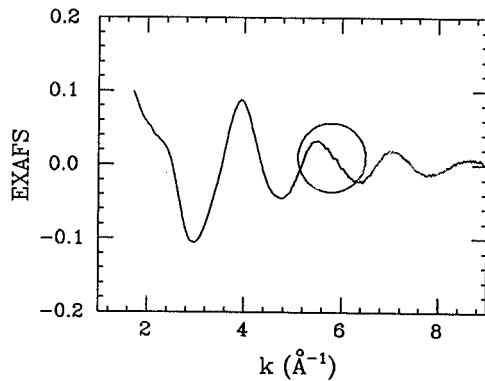


Fig. 1  
The EXAFS spectrum of a-Si:H

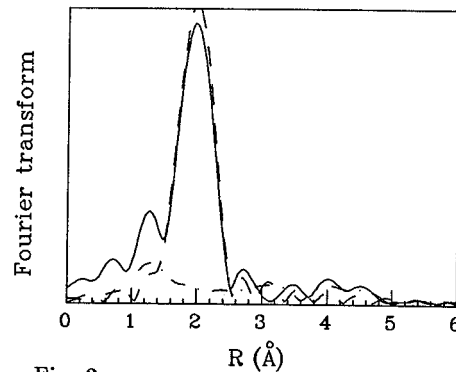


Fig. 2  
Fourier transforms of EXAFS extracted using different background models

noise of the order of  $10^{-2}$  of the EXAFS signal (Fig. 1). The distortions from the ideal sinusoidal behaviour, predicted by the EXAFS theory for a single gaussian shell, are evident; in particular we evidence (circle) the depression of the second maximum at  $\approx 5.8 \text{ \AA}^{-1}$  which corresponds to the double excitation. As we shall prove this distortion arises from the inadequacy of a smooth polynomial to account for the step-like background due to the presence of an additional edge in the absorption coefficient.

In order to separate the various contributions to the spectrum an unusual data analysis has been adopted. We have fitted directly to the absorption coefficient a signal composed of three parts:

- a smooth polynomial accounting for the average atomic cross section of the K-edge and the background.
- an oscillating signal made up of smooth,  $k$  dependent, amplitude and phase. This should account for the main EXAFS first shell signal.
- a step function with a jump of variable height at 1970 eV which should account for the double excitation.

The parametrization for the oscillating contribution b) was

$$\chi(k) = \frac{1}{k} \frac{A + \frac{D}{k^2}}{B + (k - C)^2} \sin(2kR + \phi(k)) e^{-2\sigma^2 k^2}$$

where  $R$  and  $\sigma^2$  are known structural parameters and:  $\phi(k) = F_0 + F_1 k + F_2 k^2$ . The fitting parameters were  $A, B, C, D, F_0, F_1, F_2$ , the jump for the double excitation contribution  $J$  and the coefficients of a 5<sup>th</sup> degree smooth polynomial.

The best fit was performed using the MINUIT program of the CERN library in the energy interval 1850 – 2160 eV; the small interval 1956 – 1980 eV was excluded because the step function could not reproduce the shape of the double excitation edge region.

We emphasize that the component c) was actually necessary in order to obtain a good fit in the energy region of  $\pm 50$  eV around the double excitation. The height of the jump was found to be 1.7% of the main edge jump. At the same time the use of a step-shaped model for the atomic absorption resulted in a large improvement in the EXAFS shape. In Fig. 2 we compare the Fourier transforms (FT) of the EXAFS spectra extracted using the two different background models, i.e. the FT of the EXAFS of Fig. 1 (continuous curve) and that of the EXAFS obtained subtracting the components a) and c) to the absorption spectrum (dashed curve). The former shows an unphysical spurious peak at  $R \approx 1.3 \text{ \AA}$ , a distance shorter than the first neighbours Si-Si peak while the latter does not. This peak is usually present in the FT of K-edge EXAFS spectra of any silicon material<sup>5,6</sup> extracted with the standard procedure. It is due to the residual

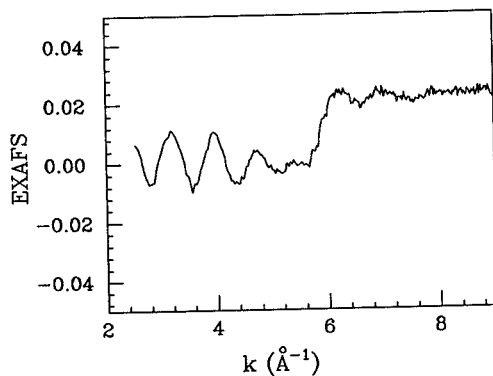


Fig. 3  
The residual spectrum

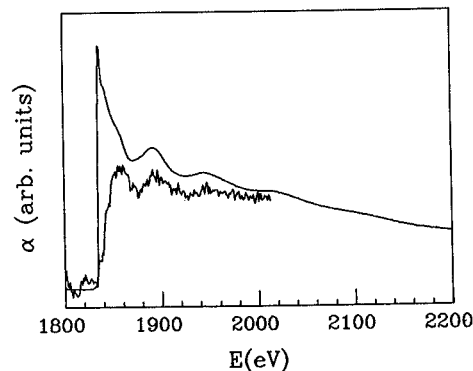


Fig. 4  
Comparison between the K-edge  
and KL-edge absorption cross sections.

low frequency left in the EXAFS by the smooth polynomial which follows gradually the double excitation edge. In Fig. 2 we also verify that the FT of the component c) after the subtraction of a smooth fitting polynomial peaks as expected at  $R \approx 1.3 \text{ \AA}$  (dot-dashed curve).

The residual signal obtained subtracting the components a) and b) from the absorption coefficient is reported in Fig. 3. We emphasize that all the features left in the spectrum are at frequencies higher than any component of the subtracted signal, therefore they cannot have been introduced by the subtraction procedure and consequently arise from physical effects. The residual signal is clearly composed of two contributions: a structural high frequency signal in the low  $k$  region and a jump at  $k \approx 5.8 \text{ \AA}^{-1}$ . In this paper we deal with this second feature. Due to its energy position, such edge can only be attributed to a channel in which both one K and one L electron are excited at the same time and will be indicated hereafter as KL-edge. Because of the energy position, such edge can only be attributed to a channel in which both one K and one L electron are excited at the same time and will be indicated hereafter as KL-edge. It is worth emphasizing however that the structural high frequency signal clearly damps out before the KL-edge, therefore all the residual after  $k \approx 5.8 \text{ \AA}^{-1}$  refers to the double excitation cross section.

As evident in Fig. 3, several oscillations are also present above the KL-edge. Such a fine structure is real, well above the noise level, and cannot have been introduced during the data analysis. It has also been detected in the spectra of other samples with a suitable signal to noise ratio.

In Fig. 4 we compare the experimental absorption cross sections of the K-edge and that of the KL-edge. The latter spectrum was shifted by 124 eV to lower energies in order to align the two thresholds and magnified by a factor of 40. The similarity between the two edges is evident. The energy onset of the KL-edge is smooth compared to the main K-edge, the first maximum occurring  $\approx 24 \text{ eV}$  above the threshold. Such smeared threshold reflects the behaviour of the cross section which changes from the adiabatic to the sudden limit in such interval of energies. We also point out that the oscillations above the KL-edge closely resembles the EXAFS oscillation of the main K-edge. This coincidence can hardly be casual: we are observing for the first time an EXAFS signal associated with a double excitation edge. As a final support to this identification in Fig. 5 we compare the EXAFS of the K-edge and that of the KL-edge extracted with the standard procedure, and their Fourier transforms in the range  $2-7 \text{ \AA}^{-1}$ . The two spectra are identical in amplitude with only a slight phase shift difference which is however not certain because of the edge position uncertainty.

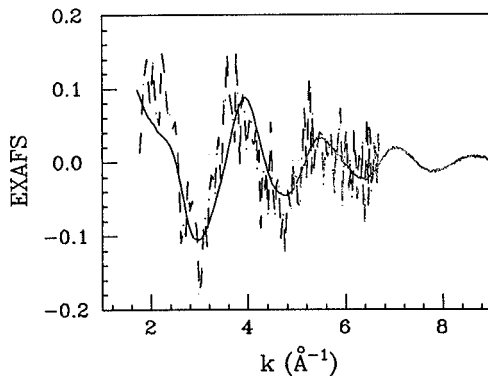


Fig. 5a  
Comparison between the EXAFS spectra  
of a-Si:H at the Si K-edge (continuous)  
and at the KL-edge (dashed)

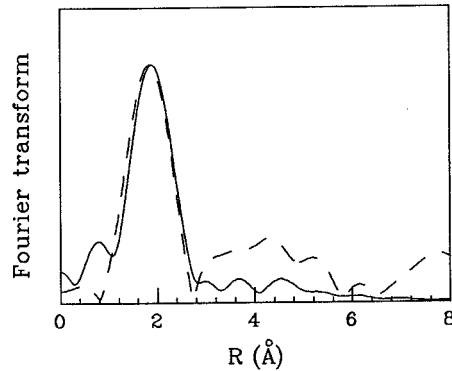


Fig. 5b  
Fourier transforms of the  
EXAFS reported in Fig. 5a

### 3. DISCUSSION

We summarize briefly the experimental conclusions.

- 1) 124 eV after the K-edge of silicon a double excitation channel opens which involve both one K and one L electron (KL-edge).
- 2) the transition from adiabatic to sudden limit takes place in an interval of  $\approx 24$  eV.
- 3) An EXAFS signal, identical to that of the K-edge, is present above the KL-edge.

Such three points allow an unambiguous identification of the process involved in the observed KL-edge. The energy position of the edge is consistent with the binding energy of a 2p electron in the  $Z+1$  approximation; the process therefore must be due to the excitation of a 1s electron to the continuum associated to a shake-up of a 2p electron. In the experimental spectrum there is no evidence for the presence of a further edge corresponding to the shake-up of a 2s electron which according to its binding energy should occur  $\approx 50$  eV above.

The existence and the shape of the EXAFS oscillation suggest that only one electron is excited to the continuum and the symmetry of the final state wavefunction is p-like ( $\epsilon p$ ) just as that for the main K-edge. Indeed the agreement in phases could not be achieved if the final continuum state symmetry were s or d-like, while, on the other hand, only a slight phase difference is expected for a p-like state because of the different self-consistent potential due to the double core hole in the KL-edge. In this way the same energy scale for the EXAFS is predicted apart from the shift of 124 eV needed to shake up the L-shell electron.

This considerations support the idea that only the shake-up process  $(1s, 2p) \rightarrow (3p, \epsilon p)$  contributes to the observed KL-edge. A more detailed account of our findings will be reported elsewhere<sup>7</sup>.

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