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MULTIELECTRON EXCITATIONS IN X-RAY-ABSORPTION SPECTRA OF a-Si:H

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Multielectron excitations in x-ray-absorption spectra of *a*-Si:H

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In this paper a detailed analysis of a multielectron excitation observed 124 eV above the *a*-Si:H *K* edge is reported. The cross section of this excitation is about 1.7% of the main edge. The onset of the transition is smooth compared with the *K* edge, but reaches the sudden limit in only about 25 eV. The excitation shows the presence of a fine structure, on its high-energy side. The dominant channel in the multielectron excitation has been identified as a $1s2p \rightarrow \epsilon_p' 3p'$ transition. Calculations in the $Z+1$ approximation within the framework of a previously proposed exchange model have shown a close agreement with the experimental data in all the transition region between the onset and the sudden limit.

I. INTRODUCTION

Since the 1960s multielectron transitions have been observed in the x-ray-absorption coefficient of atoms.[1-5] In condensed matter, excitations involving two deep core states generally occur in the region of the extended x-ray-absorption fine structure (EXAFS) oscillations, which are at least 1 order of magnitude larger; therefore they have been easily identified only in disordered systems like noble gases. Only recently, in careful systematic studies on multielectron excitations in solid by means of x-ray-absorption spectroscopy (XAS), Salem and co-workers led to the identification of multielectron excitations well above the *K* edges of Ge, Cu, Zn, and Se in a region where the EXAFS oscillations are completely damped.[6,7] They also observed multielectron excitations above the *L* absorption edge spectra of some rare earths.[8,9] Even three-electron excitations have been detected in the *K*-edge XAS of Ni by Deutsch and Hart.[10] On the other hand, in the region of EXAFS and x-ray-absorption near-edge structure (XANES) few clear experimental identifications of such multielectron excitations exist, the first being from Stern *et al.* on the x-ray spectrum of $MnCl_2$.[11]

Moreover the energy dependence of the cross section of multielectron processes is still far from being fully understood both in XAS and in XPS: indeed only few quantitative experimental and theoretical investigations on the subject exist in the literature.[12-18] Well above the transition onset the sudden approximation, generally used in XPS data analysis, is valid.[15] In such an approximation the ionization process is so rapid that the other electrons (passive electrons) do not rearrange themselves to the presence of the hole in the inner shell so that the ion may be left in excited states. At the threshold, on the other hand, the primary photoelectron leaves the atom slowly and the excited atom can relax its wave function in an adiabatic way minimizing the cross section of shake processes. As a consequence both in XAS and in XPS, the cross section of a particular correlation process is predicted to change with the excitation energy from a minimum value at threshold to the sudden approximation asymptotic value. The energy interval in which this limit is reached and the shape of the transition onset are still open questions. Carlson and Krause in an XPS investigation of atomic Ne showed that the sudden limit is reached more than 200 eV above the threshold for shakeoff processes.[16] Recently, it has been found that in Kr the shakeoff transition $1s3d \rightarrow$continuum reaches the sudden limit in only 20 eV.[17] Stohr *et al.* found that a shakeup transition originating from a bonding to antibonding orbital of N_2 on Ni(100) reaches the sudden limit within only 15 eV above the process threshold.[18] They proposed a model which describes the transition from adiabatic to sudden limit by a simple exchange picture showing that the onset energy interval is of the order of the additional shakeup energy. Their model, which assumes zero cross section at threshold, is consistent, at least qualitatively, also with the Carlson and Krause data. On the other hand, Heimann and co-workers, in very accurate systematic XPS studies of the shakeup satellites of noble gases, have shown that the cross sections of the satellites do not display any tendency to approach zero at threshold.[12-14] Such a view clearly suggests the opportunity for better theoretical and experimental investigations of the transition region, to clarify the origin and the parameters which control the different behavior found for the shakeup cross section. Finally, according to Rehr *et al.*[19] it is generally believed that every shakeup and shakeoff correlation process presents on its higher-energy side an associated EXAFS spectrum, shifted in energy with respect to the single-excitation EXAFS. But up to now no experimental evidence of such EXAFS oscillations above shakeup or shakeoff processes has been reported.

In the present paper 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 neighbors. However, as we already reported,[20] small but detectable distortions arising from two different effects are present. The first one is a residual high-frequency structural signal, mainly due to the second-coordination-shell EXAFS and to multiple-scattering effects, the second is a steplike signal 124 eV above the K edge, due to the opening of a two-electron excitation channel. In this paper we investigate in detail this second feature. We have found that at threshold the cross section of the transition approaches zero, but it reaches the sudden limit faster than the predictions of Stohr's model. Moreover, for the first time, a fine structure on the high-energy side of the multielectron excitation has been observed, and its origin is discussed in some detail. The experimental signal favors an interpretation in which only the shakeup excitation $1s3p \rightarrow \varepsilon_p' 3p'$ contributes to the cross section. Calculations in the $Z+1$ approximation agree with this picture.

II. EXPERIMENTAL AND DATA ANALYSIS

An a-Si:H sample was deposited by glow discharge on a 12.5-μm-thick Be 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 h of dedicated beam time at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris–Sud (LURE) (Orsay) on the storage ring Accélérateur Circulaire d'Orsay, by recording a large number of spectra. The averaged spectrum resulted in very good quality with a noise of the order of 10^{-2} of the EXAFS signal.

In Fig. 1 we show the EXAFS spectrum extracted from the absorption spectrum by using standard data analysis procedures. The dominance of a single-frequency signal is evident as predicted by the EXAFS theory for a single Gaussian shell. Moreover, some distortions are evident: in particular, we note (circle in Fig. 1) the depression of the second maximum at ≈ 5.7 Å^{-1} (i.e., ≈ 124 eV above the K-edge threshold). In the already mentioned previous paper,[20] we have shown that such distortion is due to the presence of a double-excitation edge in the spectrum.

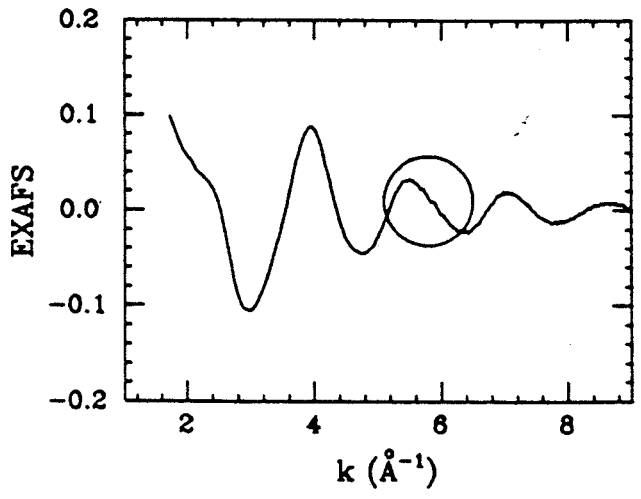

FIG. 1. EXAFS spectrum of a-Si:H extracted with the standard procedure. The circle evidences the distorsion from a single sinusoidal behavior.

In the present work we have adopted a sophisticated data analysis procedure to separate the different contributions to the absorption spectrum (EXAFS, multiple scattering, and double-electron excitations). In fact the standard methods of data analysis make strong use of the hypothesis that the smooth background around which the EXAFS signal oscillates is well described by a smooth polynomial spline, with no steplike contribution. To account for this last contribution we have fitted directly to the absorption coefficient a signal composed of three parts:

(a) A smooth polynomial accounting for the average atomic cross section of the K edge and for the background.

(b) An oscillating signal made up of a smooth k-dependent amplitude and phase. This should account for the main first shell EXAFS signal, the biggest contribution present in the spectrum.

(c) 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

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

where R (first-neighbor distance) and σ^2 (root-mean square of R) are known structural parameters; the phase function $\phi(k)$ has been parametrized as

$$\phi(k)=F_0+F_1k+F_2k^2 .$$

The fitting parameters were A,B,C,D,F_0,F_1,F_2, the jump of the double-excitation contribution J, and the coefficient of the fifth-degree smooth polynomial. The best fit was performed using the MINUIT program of the Centre Européen des Recherches Nucléaries (CERN) library, in the energy interval 1850–2160 eV; the small interval 1956–1980 eV was excluded because the step function cannot account for the line shape of the double-excitation edge region.

We emphasize that the component (c) of the signal was actually necessary in order to obtain a good fit in the region of 50 eV around the double-excitation edge. The height of the jump was found to be 1.7% of the main K-edge jump.

III. RESULTS

The use of the step-shaped model for the atomic absorption results in a large improvement of the EXAFS shape. In Fig. 2 the Fourier transform (FT) of the EX-

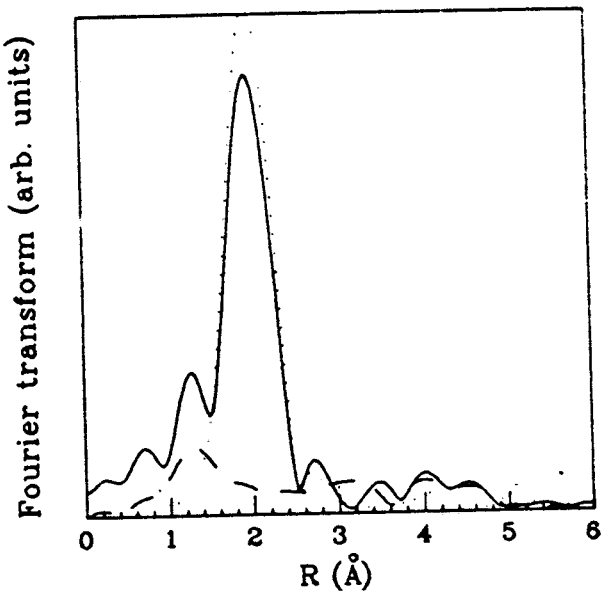

FIG. 2. Fourier transform of the EXAFS spectrum of *a*-Si:H extracted using the standard data analysis procedure (solid line) and the data analysis procedure presented here (dotted line). The dashed line shows the contribution of the steplike signal to the Fourier transform.

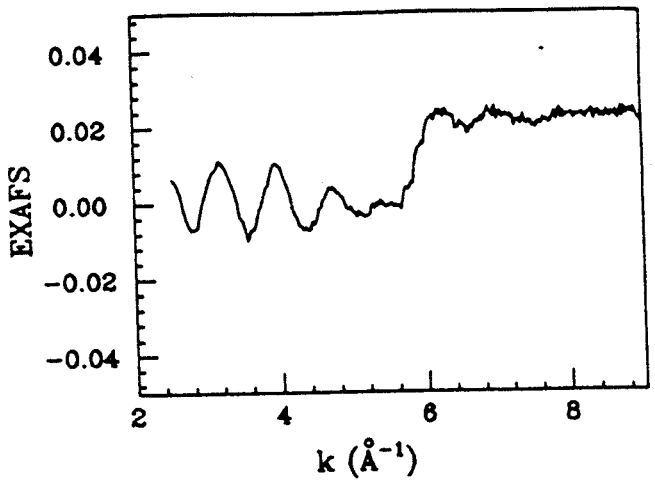

FIG. 3. Residual signal obtained after removing from the absorption spectrum the atomic background and the first shell EXAFS.

AFS spectrum obtained subtracting the components (a) and (c) from the absorption spectrum (dotted curve) and the FT of the EXAFS spectrum of Fig. 1, obtained with the standard data analysis procedures (solid curve), are compared. The latter shows an unphysical spurious peak at $R \approx 1.3$ Å, a distance shorter than the first-neighbor Si-Si peak, while the former does not. This peak is usually present in the FT of the *K*-edge spectra of any silicon material extracted with the standard procedure. It is now clear that its origin is in a low-frequency residual left in the EXAFS spectrum by the smooth polynomial used in the standard data analysis. To further verify this, in Fig. 2 we also report the FT of the steplike component (c) after fitting to it and subtracting from it a smooth polynomial in the same energy range in which the standard data analysis has been performed. As expected the FT peaks at ≈ 1.3 Å (dashed curve). This identification has a great importance in the consequences of the structural analysis of x-ray-absorption spectra at the Si *K* edge.

The residual signal obtained subtracting the components (a) and (b) from the absorption coefficient is reported in Fig. 3. This residual spectrum carries all the information present in the XAS spectrum different from the atomic background and the first shell EXAFS. We emphasize that all the features left in the spectrum are at frequencies higher than any component of the subtracted signal; they have not been introduced by the subtraction procedure and consequently arise from physical effects. The residual signal is composed of two contributions: a structural high-frequency signal in the low-k region and a jump at $k \approx 5.7$ Å^{-1}. In this paper we deal only with this second feature. Due to its energy position, such an edge can 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 the *KL* edge. It is worth emphasizing that the structural high-frequency signal damps out before the *KL* edge, so that presumably all the residual for $k > 5.7$ Å^{-1} refers to the double-excitation cross section.

As is evident in Fig. 3 a fine structure is present above the *KL* edge. It is well above the noise level and has been also detected in the spectra of other samples with a suitable signal-to-noise ratio. In Fig. 4 the experimental absorption cross sections of the *K* edge and that of the *KL* edge are compared. The latter was shifted 124 eV to lower energies in order to align the two energy thresholds. The similarity between the two edges is evident. The energy onset of the *KL* edge is smoother than the primary *K* edge, the first maximum occurring ≈ 25 eV above the threshold.

Moreover, the fine structure above the *KL* edge closely resembles the EXAFS oscillations of the main *K* edge.

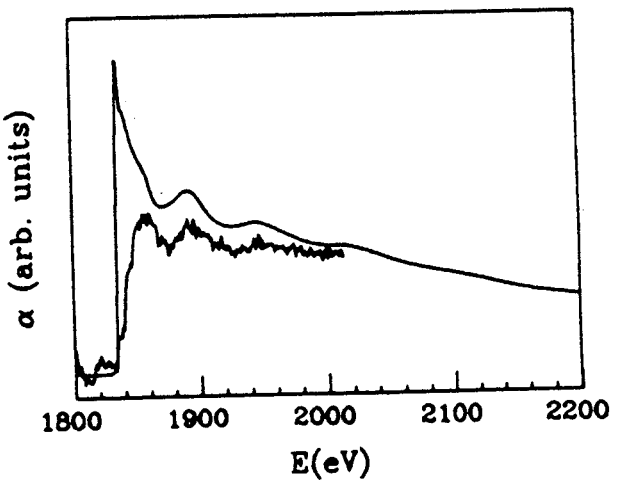

FIG. 4. Comparison between the *K* edge and the *KL*-edge absorption cross section; the latter has been shifted by 124 eV toward lower energies and magnified by a factor of 40.

This suggests the idea that we are observing an EXAFS signal associated with a double-excitation edge. As support for 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, calculated in the energy range 2–7 Å^{-1}. The two spectra and the two FT's are very similar, with only a slight phase-shift difference which can be due to the relative edge position uncertainty.

However, a second interpretation for the fine structure cannot be excluded, since the oscillations after the KL edge are in phase, in the k scale of the K edge, with the structural residual at smaller energies (Fig. 6). Therefore the signal can also be the prosecution of the structural residual above the KL edge. In such a case a beating minimum must be present in the envelope function of the structural residual around 5.5 Å^{-1}, showing the presence in a-Si:H of a splitting in the second shell distances. This would have an important consequence for its implications in the structure of a-Si:H. A definite classification of such fine structure is not possible at the moment, without looking at the behavior of other systems, and so will be reported in the future.

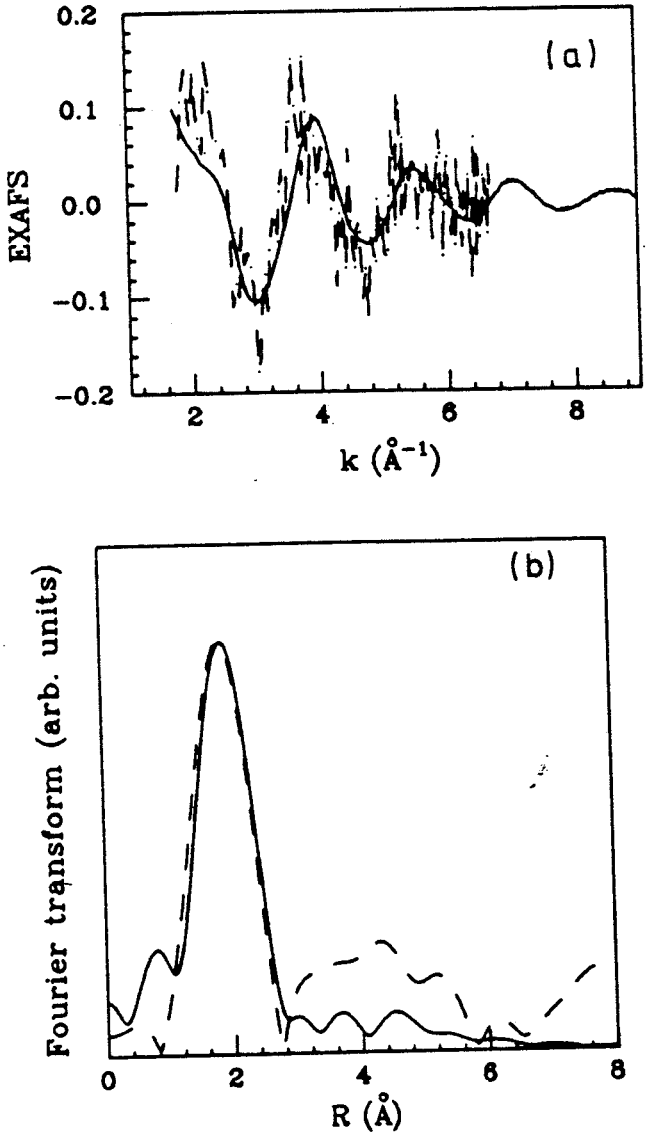

FIG. 5. (a) Comparison between the EXAFS spectra of a-Si:H at the Si K edge (solid line) and at the KL edge (dashed line). (b) Fourier transform of the spectra reported in (a).

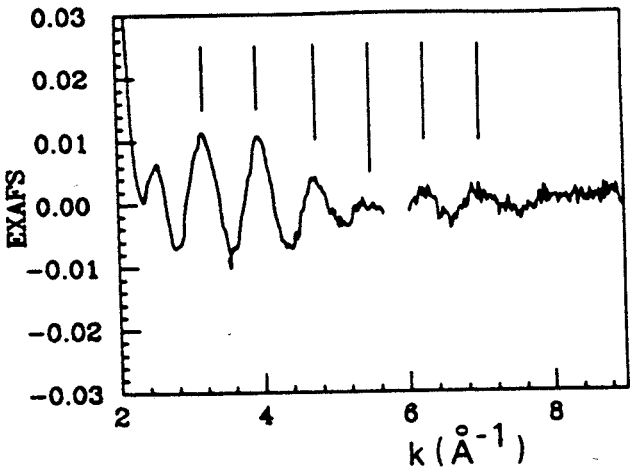

FIG. 6. Residual signal of Fig. 3 after shifting the fine structure above the KL edge towards the zero to align it with the signal present at lower k values. The region around the KL edge is not reported. The distance between the solid lines is constant and equal to 0.75 Å^{-1}.

IV. DISCUSSION

We summarize briefly the experimental conclusions:

(1) 124 eV above the silicon K edge a double-excitation channel involving both one K and one L electron (KL edge) opens;

(2) the transition from the adiabatic to the sudden limit takes place in an interval of $\approx$24 eV;

(3) a fine structure is present above the KL edge.

To classify the possible channels involved in the KL edge we will make use of atomic quantum numbers. As for the initial state, we may have either the concomitant excitation of a $1s$ and a $2p$ electron ($KL_{2,3}$ edge) or the excitation of a $1s$ and a $2s$ electron (KL_1 edge). According to the dipole selection rule, several angular symmetries can be reached from the $1s2p$ initial state: $p'p'$, $s'd'$, $s's'$. On the other hand, only $s'p'$ channels are allowed in the KL_1 case. Assuming the ground state of silicon as $1s^2 2s^2 2p^6 3s^2 3p^2$, the allowed lowest shakeup transitions with at least one electron in the continuum are those reported in Table I, together with their energy positions calculated in the $Z+1$ approximation. The experimental energy position of the KL edge is consistent only with transitions involving electrons from the $1s2p$ initial state, and therefore will be indicated hereafter as the $KL_{2,3}$ edge. There is no evidence in the experimental spectrum of the presence of any shakeup of a $2s$ electron, which according to its binding energy should occur $\approx$57 eV above the $KL_{2,3}$ edge.

TABLE I. Possible initial and final states for the multielectron transitions involving K and L levels. The energy positions are evaluated in the $Z+1$ approximation.

Process	Initial state	Final state	$Z+1$ energy (eV)
1	$1s2p$	$3p'\varepsilon'_p$	121.7
2	$1s2p$	$4s'\varepsilon'_d$	121.5
3	$1s2p$	$3d'\varepsilon'_s$	121.9
4	$1s2p$	$4s'\varepsilon'_s$	121.5
5	$1s2s$	$4s'\varepsilon'_p$	179
6	$1s2s$	$3p'\varepsilon'_s$	179

The final state of the $KL_{2,3}$ transition for each process of Table I can have also the bounded electron in higher n' levels. Moreover, the excitation to such higher n' states is not relevant since its cross section decreases sharply with increasing n: in the case of Kr, for example, the $1s3d \rightarrow 5d'\varepsilon'_p$ shakeup transition is only 10% of the $1s3d \rightarrow 4d\varepsilon'_p$ one.[21] For the same reason channels 2 and 4 in which an electron is shaken up to a $4s$ level have a negligible cross section. Therefore only channels 1 and 3 can contribute to the $KL_{2,3}$ edge. Moreover, all channels of Table I are at the limit of Rydberg-like series due to excitation of both electrons to bounded states. Note that the experimental spectrum does not show any sharp peak at the threshold, due to such transitions.

From Table I it is evident that it is not possible to discern between process 1 and 3 on the basis of the $KL_{2,3}$-edge energy position. However, if the fine structure above the $KL_{2,3}$ edge is really a first shell EXAFS signal associated with the $KL_{2,3}$ excitation, the good matching of the phases between the K edge and the $KL_{2,3}$ edge EXAFS would indicate that the symmetry of the final-state wave function is p-like as that of the main K edge. In fact in such a case only a small change of the central-atom phase shift should be present resulting from the difference in the central-atom final-state potential, which has a double hole in the $KL_{2,3}$ case, instead of a single hole in the K-edge case. An upper limit to this change can be estimated, from the tables of Teo and Lee,[22] to be about 0.05 rad. Such a small phase shift can be easily accounted for by a E_0 shift and therefore is outside the present sensitivity. 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, as illustrated in Figs. 4 and 5. On the other hand, an agreement in phases could not be achieved if the final continuum states were s- or d-like. These considerations bring us to the hypothesis that the shakeup process 1 ($1s2p \rightarrow 3p'\varepsilon'_p$) is the main contribution to the observed KL edge.

To unambiguously verify this hypothesis and to have a deeper insight in the origin of the $KL_{2,3}$ edge, let us now look to the cross section of the process reported in Table I. In the sudden limit, the cross section $\sigma^{KL}_{\text{sudden limit}}$ of the $1s2p \rightarrow 3p'\varepsilon'_p$ process is given by

$$\sigma^{KL}_{\text{sudden limit}} = \sigma^K \,|\, \langle 2p \,|\, 3p' \rangle \,|^2 , \tag{2}$$

where σ^K is the cross section of K edge. We have calculated a value of 2.8×10^{-3} for the overlap integral $|\langle 2p \,|\, 3p' \rangle|^2$, by using Clementi and Roetti wave functions, in the $Z+1$ approximation. Taking into account the degeneracy of the allowed final states, which is 4 for an s^2p^2 initial-state configuration, we get the value of 1.2×10^{-2} for the ratio between the shakeup and the K-edge cross sections. In spite of the large approximation made, in using atomic orbitals in a solid-state case, a fairly good agreement is achieved with the experimental cross section which amounts to 1.7×10^{-2}.

From the experiment it appears that the $KL_{2,3}$-edge cross section changes from zero at threshold up to the sudden limit value, reached at $\approx$24 eV above the threshold. Estimates of the energy interval needed to reach the sudden limit are difficult to account for in the framework of a one-electron theory. A full quantitative interpretation should be evaluated within the framework of the configuration interaction. At first, we assume vanishing off-diagonal terms between different electron configurations. In this case the total cross section is given by the sum of the cross sections of each channel. Stohr *et al.*[18] have shown that—even if the cross section of a shakeup process, in accordance with the Wigner threshold law, is different from zero since threshold—in some cases, such as our $1s2p \rightarrow 3p'\varepsilon_p$ transition, the Pauli principle requires the cross section to vanish at threshold. In fact, approximating both the initial and final states as 2×2 Slater determinants the cross section is given by the square modulus of the difference between a "direct" term and an "exchange" one. Well above the excitation threshold the exchange term vanishes and the cross section reaches its sudden limit value. Vice versa, at the threshold, the two terms approach the same value and the cross-section zero. In the case of the $1s2p_1 \rightarrow 3d'\varepsilon'_s$ channel, it can be easily shown that the cross section has no exchange term. So we would expect to observe a sudden onset in correspondence of its threshold. Since in the spectrum there is no evidence of a very fast onset channel, we exclude that it actually contributes significantly to the observed $KL_{2,3}$ edge.

To describe the cross-section energy dependence from the adiabatic to the sudden limit in the cases where the exchange term is present, Stohr *et al.*[18] approximated the continuum wave function as a plane wave (PW) and the initial-state wave function with hydrogenic states, predicting the following behavior:

$$\sigma = \sigma_{\text{sudden}} \,|\, 1 - \Delta E / E_{\text{exc}} \,|^2 . \tag{3}$$

In this equation, ΔE is the satellite energy above the main excitation and E_{exc} is the primary photoelectron energy in excess to the main single-excitation edge. This formula predicts an energy interval between adiabatic and sudden limit of the order of a few times the additional shakeup energy of the process. This result does not agree with our findings on the $KL_{2,3}$ edge in Si. We believe that the reliability of the Stohr *et al.* calculation is strongly affected by the use of the plane-wave approximation for the final state, since as already pointed out, both PW and orthogonalized-plane-wave (OPW) approximations are inadequate in calculating photoionization cross sections.[23]

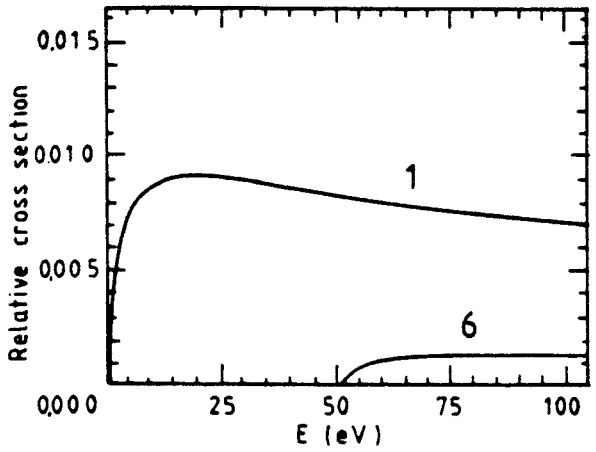

FIG. 7. Calculated cross sections, normalized to the K-edge cross section for the processes 1 and 6 of Table I.

We have computed the cross section of some processes of Table I, using more realistic wave functions. The Clementi and Roetti Si wave functions have been assumed as initial-state wave functions. The final-state continuous wave function has been calculated solving the Schrödinger equation for one electron in the Coulombic field of the others. The equation was numerically integrated from the origin up to the first maximum of the wave function and there matched to the solution obtained in the Wentzel-Kramers-Brillouin approximation. The Coulombic potential was built in a $(Z+1)$-like way. Namely, because L electrons are affected also by the second hole in their shell, they were approximated by wave functions of the S atom. An additional electron was placed in the M shell to account for the screening of the residual hole by the valence electrons of the solid.

Figure 7 reports the so-calculated cross section for the excitation channels 1 and 6. The cross sections have been multiplied by the initial- and final-state degenerations, and normalized to the main K-edge cross section. We emphasize how, in agreement with the experiment, the $1s,2p \rightarrow 3p'\varepsilon'_p$ transition has a very fast onset, reaching the limiting value of the sudden approximation in less than 20 eV. From the calculation it results also that the fast onset interval is a direct consequence of the relaxation of the inner-shell electrons and cannot be accounted for by any plane-wave approximation. In fact, we verified that, neglecting the collapse of the K and L shells' passive electrons, the fast onset cannot be reproduced in the calculation. In Fig. 7 we also verify that the dominant transition involving the excitation of the $2s$ electrons is small and can be hardly observed. All these results confirm that the $1s2p \rightarrow 3p'\varepsilon'_p$ transition is the only one appreciably present in the spectrum.

As for the configuration interaction, in the first-order perturbation theory the mixing coefficient between the fundamental channel $1s2p \rightarrow 2p'\varepsilon'_p$ and the $1s2p \rightarrow 3p'\varepsilon'_p$ can be approximated as:[24]

$$c \approx \frac{|\langle \Phi^N_{(2p'\varepsilon'_p)} | V | \Phi^N_{(3p'\varepsilon'_p)} \rangle|^2}{\Delta E}, \tag{4}$$

where V is the Coulombic potential felt by the photoelectron and $\Phi^N_{(2p'\varepsilon'_p)}$ and $\Phi^N_{(3p'\varepsilon'_p)}$ are the N-electron wave functions for the indicated electron configurations. We have evaluated this coefficient to be of the order of 10^{-2}. This implies a change in the cross section of at maximum 10^{-3} of the total cross section, i.e., of the order of 10% of the observed multielectron excitation cross section, and therefore its effects can be completely neglected in the present work.

V. CONCLUSIONS

The existence of a small but detectable signal due to a multielectron transition in XAS spectra of a-Si:H is the main result of this paper. The energy position, intensity, and the extension of the energy interval for the onset of the sudden region give strong support to the identification of the structure as due to the $1s2p \rightarrow 3p'\varepsilon'_p$ shakeup transition. The $Z+1$ approximation, within the framework of Stohr's exchange model, accounts for the main characteristics of the KL edge observed. In spite of the strong approximation used, our calculations are able to single out the rapidity of the onset, giving a good quantitative estimate of the transition region between the adiabatic and the sudden limit.

A definite explanation of the fine structure present on the high-energy side of the shakeup transition cannot be given this time. It can be either the persistence of the structural residual signal or the EXAFS associated with the shakeup transition. In both cases there will be important physical consequences. A more detailed investigation of such an aspect on other systems is in progress.

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