Excitation-Energy Dependence in the $L_{2,3}$ Fluorescence Spectrum of Si

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The $L_{2,3}$ emission spectrum of *c*-Si, excited by monochromatized synchrotron radiation, has been recorded with a 5-m Rowland spectrometer. Dramatic spectral changes are observed as the excitation energy is varied from the 2*p* binding energy up to 144 eV. It is proposed that a spectator electron, close to the bottom of the conduction band, influences the emission spectrum. The observations suggest that interband shakeup is important in the excitation process, and that a population of low-lying levels, via initial-state shakeup, influences the high-energy-excited Si *L* emission spectrum.

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Soft-x-ray emission (SXE) spectra of light *s-p* bonded elements have been interpreted successfully in terms of one-electron band structure calculations and the final-state rule. The intensity of the radiation emitted as an electron from the valence band fills an initial core hole provides a measure of the angular-momentum-selected partial density of states (PDOS) localized around the core hole. Second-order effects include an enhancement of the intensity close to the Fermi level in nearly-free-electron metals, associated with the change of screening when the core hole is annihilated. Also, a low-energy tailing due to the finite lifetime of the final states has been observed. SXE are also known to be modified by multiple excitations occurring *during the emission process*.

High-energy-electron–excited SXE spectra of atoms, molecules, and solids with highly localized *d* or *f* valence electrons exhibit a complex satellite structure due to local multiple valence excitations in the initial states. The satellites often overlap the main lines, and selective excitation is needed to make a quantitative interpretation feasible. As has been demonstrated in recent years, the tunability of monochromatized synchrotron radiation (MSR) makes it possible to study the excitation-energy dependence of satellites associated with multiply excited states.[1-5]

For the light elements with strongly overlapping orbitals and delocalized valence electrons there has, to our knowledge, been no previous experimental results which suggest that multiple excitations *during the creation of the core hole* should have an effect on the SXE main bands. Theory has generally ignored the possibility since the time scale for core-hole screening is much shorter than the core-hole lifetime. Nonselectively excited spectra have been thought to correspond to the decay of fully screened pure core holes.

In contrast to expectations based on theory and previous results, we have observed major modifications of the Si $L_{2,3}$ emission spectrum, occurring when the spectrum is excited by MSR in the 96–152-eV energy range, the vicinity of the $L_{2,3}$ excitation threshold (100 eV). This is the first demonstration of excitation-energy dependence of the main-band SXE for a delocalized *s-p* bonded system, and the first such study in this photon energy range.

Currently the physical significance of the observations is not fully understood. However, we will put forward a tentative interpretation that we hope can serve as a starting point for a more quantitative discussion. We will argue that the modifications of the spectrum occur when electrons are injected into states coincident in energy with the bottom of the conduction band. Close to threshold these levels are reached by direct transitions from the core level, and at higher energies the states are populated by shakeup processes. Our results suggest that spectator electrons either substantially modify the wave function of the valence electrons, or have a large impact on dynamics of the emission process.

The experiment was carried out at beamline U10A at the National Synchrotron Light Source at Brookhaven National Laboratory. A recently constructed monochromator, based on a focusing toroidal mirror and a normal-incidence transmission grating,[6] was used to produce the MSR. For the present energy range we used a 1000-line/mm grating, providing exciting photons in a 4-eV energy band pass. Intensity from higher orders of diffraction and white-light background was estimated to be less than 15% of the first-order intensity.

The emission spectra were recorded in a Rowland spectrometer, employing a toroidal grating with a major radius of 5 m and 600 grooves/mm, mounted at 86° angle of incidence. The width of the entrance slit was chosen to give 0.2-eV resolution. The detector is a mounted-channel-plate image intensifier, coupled via fiber optics to a charge-coupled-device diode readout system. We estimate the self-absorption to have only a small impact on the main emission band, and to be irrelevant for the study of the emission-band changes. A detailed description of the beamline and the spectrometer is given in Ref. 7.

In Fig. 1 we show $L_{2,3}$ emission spectra of crystal Si

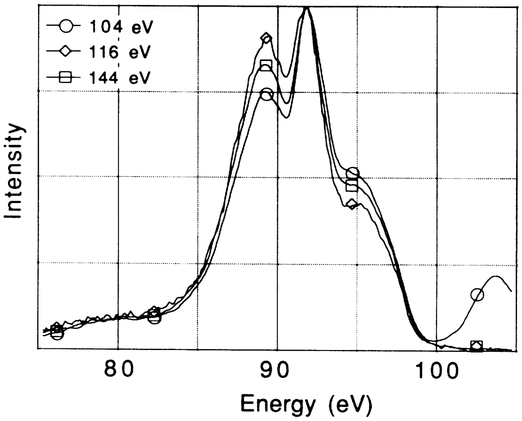

FIG. 1. Si *L* emission excited by 104-, 116-, and 144-eV photons. The spectra have been normalized to match at the most intense peak. The extra peak in the 104-eV excited spectrum is due to elastically scattered photons.

excited at 104, 116, and 144 eV. The spectrum excited at 144 eV resembles the high-energy-electron–excited spectrum, which has been the subject of several studies over the years.[8–12] The main emission band is considered to be well described by calculations based on plane waves[13,14] as well as molecular orbitals.[15] Three pronounced peaks are seen at 89, 92, and 95 eV, in accordance with the one-electron approximation, and the notion of a mapping of the 3*s* PDOS. The low-energy peak is attributed to low-lying 3*s* states, the 92-eV peak is associated with a DOS maximum with *s*-*p* hybridization, and the high-energy peak is associated with a DOS maximum, which has a dominating 3*p* contribution. The low-energy tailing of the spectrum is believed to be caused by the finite lifetime of the valence holes and the weak low-energy hump is associated with multiple electron excitations accompanying the filling of the core hole.[16]

As is seen in Fig. 1, the SXE is substantially dependent on the excitation energy when it is tuned below 144 eV. To monitor the changes we show the peak height ratios as a function of excitation energy in Fig. 2.

Many earlier analyses of excitation-energy dependence of SXE from localized systems preserve the one-electron picture for the SXE process. The tunability of MSR is used to select initial states from the ensemble excited by high-energy electrons, and the changes in the SXE closely relate to the energy dependence of the excitation cross sections for the various states. The impact on SXE spectra of a local extra valence hole,[1] as well as a local extra electron,[2] has been studied in the gas phase.[3] SXE spectra of solid-state systems with highly localized *d* valence orbitals exhibit a related behavior due to atomiclike coupling between a core and valence hole,[4] or between a core hole and an excited electron.[5]

States of this type in Si would correspond to $2p3s$ or $2p3p$ double-hole configurations, or to states where the excited *s* or *d* conduction-band electron couples quasiatomically to the core hole.

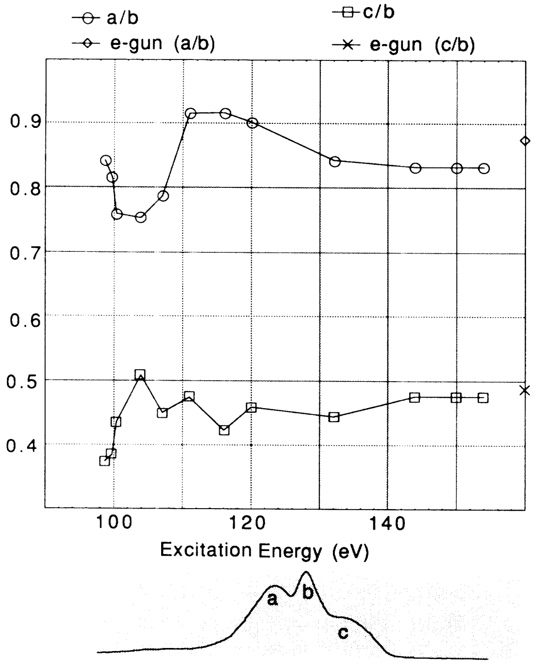

FIG. 2. Peak height ratios as a function of excitation energy. The peaks are denoted according to the scheme below the graph. The cross and the diamond symbols placed at 160-eV excitation energy refer to the spectrum excited by 2-keV electrons.

Close to threshold the Si *L* emission is changing rapidly with excitation energy, as is seen in Fig. 2. A change of excitation energy on the order of 0.5 eV produces a dramatic effect, even though the width of the monochromator is as much as 4 eV. With decreasing excitation energy the low- (*a*) and high- (*c*) energy peak intensities rapidly increase and decrease, respectively, compared to the middle peak (*b*). Below we briefly discuss this behavior of the spectrum, when excited close to threshold.

The rapid change suggests that the injection of an electron into states close to the bottom of the conduction band substantially modifies the x-ray spectrum. This could only be accomplished if the extra electron persists as a spectator close to the core hole during the process. The lifetime width of the 2*p* hole in Si has been estimated to be 100 meV,[13,17] based on line-broadening analyses. This is probably an overestimate due to the neglect of other broadening mechanisms. Recent calculations on the light metals[18] suggest that the lifetime broadening is an order of magnitude less. Only extremely low conduction-band states correspond to a kinetic energy sufficiently low to make localization important even at a lifetime broadening of 10 meV. A coupling between the core hole and the excited electron seems necessary to provide the localization. Observation of a core exciton state has been reported,[19] but the binding energy implies an electron envelope radius around 15 Å, probably too much for the electron to have any local impact on the valence electrons. In our studies of Si we do not observe structure within the band gap, except in heavily *n*-doped samples, where recombination from impurity states is a likely explanation for the observed structures. Excitonic effects within the conduction band have been considered to explain x-ray-absorption data,[20] and may be associated with the localization mechanism that we are seeking. An explanation of *LVV* Auger satellites in terms of decay of quasiatomic $2p^5 3(sp)^4 3d^1$ states has also been put forward.[21]

The spectator electron can affect the SXE spectrum either via the influence on the final-state valence-electron wave functions, or via an impact on the dynamics in the emission process. An analysis of the interaction is beyond the scope of this paper. We point out that the first interpretation implies that the spectral changes are directly related to the interaction between a slow conduction-band electron and the valence band. This indicates that theories of soft-x-ray absorption and inverse photoemission that ignore valence-electron rearrangement have limited applicability. The second interpretation deals with the dynamic response of the electron cloud to the switching of the core-hole potential. No such effects have earlier been considered necessary for the description of the Si spectrum.

We now turn our attention to the behavior at higher excitation energies. As is seen in Fig. 2, the peak height ratios have local extremes at around 104 eV, so that similar changes occur at higher as well as lower energies. This leads us to the view that electrons are injected close to the conduction-band edge by mechanisms different from direction excitation at energies above 104 eV.

In an extended system high-energy excitation allows shakeup to populate core holes with additional interband excitations, to populate exciton levels, and to create initial states with plasmon excitations.

We can immediately rule out the creation of plasmons, subsequently decaying into locally excited states. This is thought to be the most important population channel for core excitons, seen in high-energy-excited spectra.[19] At the present excitation energies, however, the cross section for plasmon excitation is negligible.[22] We propose that interband shakeup populates electronic levels close to the bottom of the conduction band, similar to those excited close to threshold.

Interband shakeup is seen in photoemission as an asymmetry in the line shape and a tailing towards higher binding energies. The excitation-energy dependence is difficult to study due to inelastic scattering of the photoelectrons, especially problematic at low electron energies. From molecular and atomic photoemission spectra it is known that the excitation-energy dependence of shakeup processes can be complex. The a/b ratio maximum around 116 eV suggests a resonance in the cross section for the associated shakeup process. The c/b ratio is changing by only a small amount in the same energy region, indicating that the states populated via shakeup are not equivalent to the threshold excited states.

The current interpretation implies that interband shakeup is an important process in core excitation at our energies. Consequently, this process should also be seen in the soft-x-ray-absorption spectrum of Si. A broad structure around 120 eV, commonly referred to as a *p-d* maximum,[23] may have a substantial shakeup contribution.

The peak height ratios seem to reach an asymptotic value around 144 eV. Spectra excited up to 160 eV are equivalent within the present level of accuracy. Our interpretation is that the sudden limit is reached for the population of the relevant shakeup states. Consequently, the high-energy-excited *L* emission spectrum of Si is distorted by the decay of states affected by the spectator electron.

The above discussion provides, we believe, the first steps towards an understanding of the excitation-energy dependence of the Si *L* emission spectrum. However, at this stage alternative explanations cannot be excluded, and we briefly mention some other attempts to understand our results.

As mentioned above local core-valence holes are not likely to exist in the delocalized Si system. The conclusion is supported by the observed lack of spectral change when passing the 2*s* excitation threshold (150 eV). The 2*s* holes created above 150 eV mostly decay via the $L_1L_{2,3}V$ Coster-Kronig process, providing 2*p* holes with an additional valence vacancy. The results show that this vacancy has no significant impact on the main $L_{2,3}$ SXE spectrum. The resemblance between the electron- and 144-eV-photon-excited spectra also corroborates the conclusion, since the shakeoff probability, slowly reaching the sudden limit,[24] is likely to change above 144 eV.

Direct localization due to quasiatomic $2p3d$ coupling high up in the conduction band as mechanism for the resonant behavior around 116 eV may be considered. Though such a coupling has been proposed to explain *LVV* Auger satellites,[21] we do not think that an excited electron, 16 eV above the *L* edge, would be localized enough to account for our observations.

Threshold-excited SXE exhibits dynamic effects, beyond the reach of theories that separate the excitation and emission processes. The general development of inelastic x-ray scattering into fluorescence, via resonances close to core ionization limits, has been studied.[3,25,26] We argue that the observed changes in the Si *L* emission are not influenced by inelastic scattering. The number of possible energy-loss mechanisms due to the width of the valence band and the width of the MSR would smear out the intensity from inelastic scattering and rule it out as a mechanism responsible for the spectral changes occurring. Also we observe changes further away from threshold than should be expected from inelastic scattering theory.

In conclusion, we have presented the excitation-energy dependence of the $L_{2,3}$ emission spectrum of *c*-Si. Dramatic changes in the spectral shape have been observed, which indicates that locally inequivalent initial states are populated up to 44 eV above threshold. Although the details of the spectral changes are not understood, we have put forward a tentative interpretation in terms of population of levels close to the bottom of the conduction band. The levels are thought to be populated directly at threshold, and via interband shakeup at higher energies. A spectator electron either interacts with the final-state valence-electron wave function, or influences the dynamics of the emission process. Our interpretation implies that interband shakeup is an important excitation mechanism, and that the high-energy-excited spectrum is distorted by local excitations.

We hope that our results will serve as a theoretical challenge and that our arguments can be a starting point for a more quantitative discussion. The study of the excitation-energy dependence of SXE spectra will, we believe, lead to a better understanding of core-hole excitation-emission dynamics.

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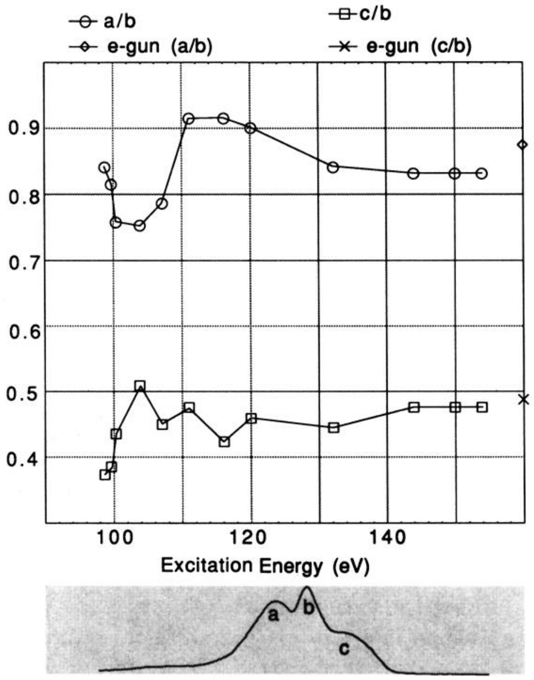

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