

Simple Calculation of $L_{II,III}$ Absorption Spectra of Na, Al, and Si†

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The shape of soft x-ray absorption spectra extending 100 eV above the $L_{II,III}$ x-ray threshold is calculated for Na, Al, and Si using a simple orthogonal plane-wave final state including backscattering from near neighbors, and hydrogenic-core wave functions. Comparison with synchrotron-radiation absorption and newly measured electron energy-loss spectra shows good agreement between the present simple calculation and experimental data.

We were led to this calculation of $L_{II,III}$ absorption spectra by an inelastic electron-scattering experiment performed with a newly constructed spectrometer. The experiment consists of transmitting a monoenergetic electron beam with 300 keV kinetic energy through thin (500–1000 Å), self-supporting aluminum foils and detecting the energy loss. By the use of a narrow-energy-pass analyzer we are able to measure directly the number of electrons per unit time that lose a given amount of energy in the sample. By select-

ing the scattering angle we can measure energy-loss spectra as a function of momentum transferred in the inelastic collision. The energy-loss resolution and the momentum-transfer resolution are variable. For the present experiment we chose an energy-loss resolution of 0.25 eV and a momentum-transfer resolution of 0.1 \AA^{-1} . The beam intensity was 10^{-8} A . Details of the spectrometer will be published elsewhere.¹

The differential scattering cross section per unit energy loss per unit solid angle for fast electrons transmitted through solid samples is²

$$\frac{d^2\sigma}{dE d\Omega} \propto q^{-4} \sum_f |\langle \psi_f | \sum_j \exp(i\vec{q} \cdot \vec{r}_j) | \psi_0 \rangle|^2 \delta(E_f - E_0 - E), \quad (1)$$

which can be rewritten²

$$\frac{d^2\sigma}{dE d\Omega} \sim q^{-2} \text{Im}\epsilon^{-1}(\vec{q}, E), \quad (2)$$

where ψ_f is a many-electron final state, ψ_0 the initial state. The sum on j is over all electrons in the solid. E_f and E_0 are the final and initial energy of the sample, respectively; E is the energy loss and \vec{q} is the momentum transfer. $\epsilon(\vec{q}, E)$ is the generalized longitudinal dielectric response function for the solid. For small momentum transfer ($q \approx E/c$), ϵ is equivalent to the optical or transverse dielectric constant. Thus for forward scattering, an electron-scattering experiment measures the more frequently encountered optical dielectric constant.

In the present experiment we measured the forward-scattering energy-loss spectrum of aluminum from 70 to 170 eV. In this region the real part of the dielectric constant $\epsilon_1 \approx 1$ and the imaginary part $\epsilon_2 \ll 1$. Thus from Eq. (2) the scattering cross section is a direct measure of ϵ_2 .

In Fig. 1 we show for comparison the DESY synchrotron-radiation-absorption data covering the same energy region.³ The two curves are not strictly comparable since the synchrotron data are a measurement of the absorption coefficient α . In this energy-loss region $\alpha \sim E\epsilon_2$. When our data are multiplied by E , the agree-

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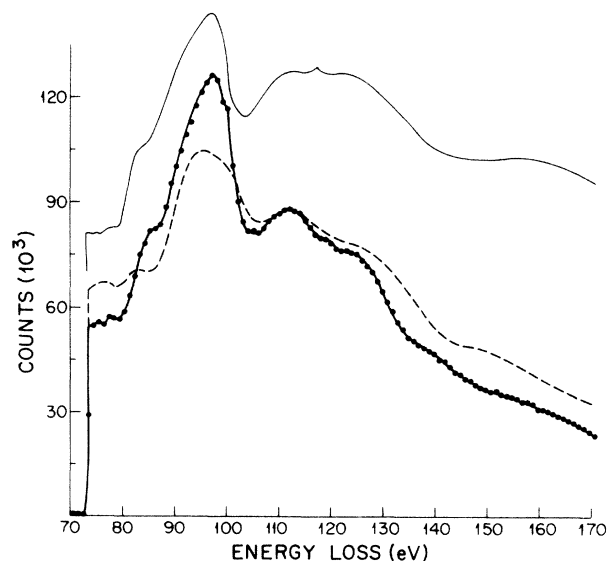


FIG. 1. $L_{II,III}$ absorption spectrum of aluminum. Solid circles, ϵ_2 measured by electron energy-loss experiment; dashed line, present calculation of spectrum; solid line, absorption coefficient of synchrotron radiation—displaced upward for clarity.

ment is quite good.

The $L_{II,III}$ aluminum spectrum has been measured by several groups,³⁻⁶ but little theoretical work has been done to explain the large wide peaks seen in the spectrum. (We are not concerned here with the actual $L_{II,III}$ or L_I threshold shape which has been the subject of much discussion.⁷) The plasmaron theory of Hedin and Lundquist⁸ can explain the positions of much of the observed structure in aluminum, but no calculation of the actual spectrum was made. In order to explain our energy-loss spectrum, we propose the following simple model.

We evaluate the cross section in the one-electron approximation and take for ψ_0 the $2p$ core state of Al. To make the calculation particularly simple we take our core wave functions⁹ to be hydrogenic, with the effective charge seen by each state chosen so as to give the proper binding energy. We compute ψ_f by perturbation theory using as a first approximation an outgoing plane wave orthogonalized to the occupied core states of the excited atom. The density of states consistent with this approximation is that of a free-electron gas. The zero of kinetic energy for the final state is taken at the bottom of the conduction band. The next correction to ψ_f will include the fact that the absorbing atom is in a regular crystal lattice, giving rise to band structure. A simple way of including band-structure effects was proposed by Shiraiwa, Ishimura, and Sawada¹⁰ and has been used by several authors to explain broad structure above deep x-ray thresholds in crystals.¹¹ This structure is usually called EXAFS (extended x-ray absorption fine structure). The idea is to simply add to the outgoing electron wave function its backscattered amplitude from all other atoms in the neighborhood. When the backscattered waves interfere constructively at the position of the excited atom, the optical absorption is increased, and destructive interference reduces the absorption. Thus the backscattering modulates the transition strength. This elementary approach appears in fact to be a simple way of including both Coulomb and band-structure effects in the calculation of soft x-ray absorption spectra.

To clarify the origins of the overall spectral shape, we present the calculation in two steps. First, we shall ignore the backscattering and calculate the free-electron absorption. We do this by expanding the exponential operator in the cross section formula and keeping only the dipole term. The transition then occurs between the p

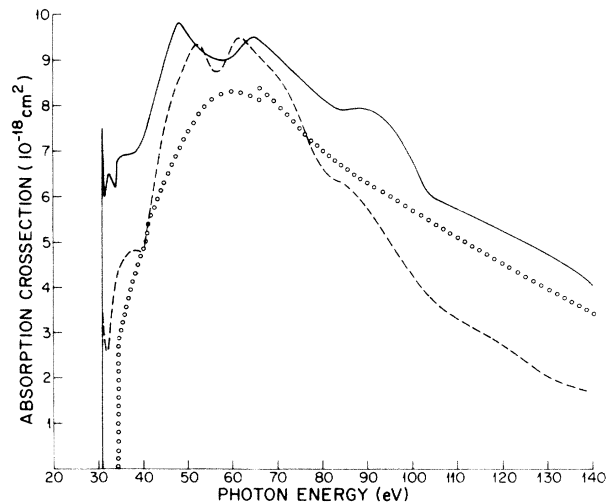


FIG. 2. $L_{II,III}$ absorption spectrum of sodium. Circles, atomic calculation of McGuire including L_I threshold at 66 eV which we neglect; dashed line, present calculation; solid line, absorption cross section measured by synchrotron-radiation absorption.

core state and s and d partial waves in the conduction band, just as for optical absorption. The resulting spectrum has a shape similar to the atomic calculation of McGuire¹² for sodium, shown in Fig. 2 (with the exclusion of the L_I edge). The shape consists of a sharp threshold at the energy of a transition from a $2p$ core state to the Fermi surface, followed by a gradual rise and then a slow decline with increasing energy. This rise above threshold is due to the "centripetal barrier" for p -to- d transitions and is a well-known atomic phenomenon. We believe that this effect is the chief explanation for the broad hump above $L_{II,III}$ thresholds and that all observed structure is merely a modulation of this transition strength due to the crystal structure.

Next, we must include the effect of backscattering. Shiraiwa has done this for the case of a weak periodic field using muffin-tin atomic potentials and the Born approximation for the scattering amplitude. The free-electron absorption is modulated by multiplication by the factor $1 + g(k)$, with

$$g(k) = \frac{f(k)}{k} \sum_s \frac{N_s}{r_s^2} \exp(-\mu r_s) \sin(2kr_s), \quad (3)$$

where k is the wave vector of the outgoing electron, the sum is over shells of atoms equidistant from the excited atom, N_s is the number of neighbors at a distance r_s from the excited atom,

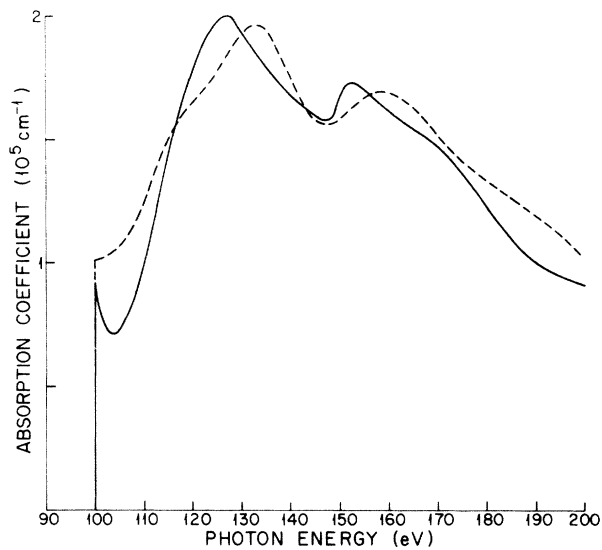


FIG. 3. $L_{II,III}$ absorption spectrum of silicon. Solid line, absorption coefficient measured by synchrotron-radiation absorption; dashed line, present calculation.

μ is a damping factor which accounts for the finite lifetime of the excited electron, and $f(k)$ is the backward scattering amplitude computed in the Born approximation for a scattering well of radius a and depth V_0 . In calculating fine structure above K x-ray thresholds, Shiraiwa assumed the matrix element was nearly constant. In computing the $L_{II,III}$ spectra we have included the variation of the matrix element with energy. The position and shape of the fine structure depends primarily on the crystal structure. We therefore chose Al, Na, and Si each with a different crystal structure and a weak periodic field to test the validity of the model. For aluminum the a of the well could be varied from 0.2 to 0.5 Å without qualitatively changing the fine structure. The spectrum was equally insensitive to μ , which was arbitrarily set equal to 0.3 \AA^{-1} .¹³ The amplitude of the modulation then depended solely on V_0 which we regarded as a free parameter. Figure 1 shows the computed result for Al which has an enhancement of 10% at 100 eV due to backscattering. Because of the simplicity of our model it was not felt worthwhile to determine any parameters by a maximum-likelihood analysis.

Figure 3 contains our model applied to the synchrotron-radiation-absorption data on silicon obtained by Gähwiller and Brown.⁶ In computing the background shape we chose $a=0.2 \text{ \AA}$, $\mu=0.4 \text{ \AA}^{-1}$ and found we could achieve better agreement by increasing the radius of the $2p$ core state by

5% over the hydrogenic value. The fine-structure enhancement at 136 eV is 15%. The zero of kinetic energy for the final-state electron is taken at the bottom of the valence band.¹⁴

In Fig. 2 we compare our calculation in sodium with the synchrotron data of Haensel *et al.*³ Our model predicts a background continuum absorption which is too sharply peaked (even though we have allowed the radius of the $2s$ core and $2p$ core states to be decreased by 15% and 20%, respectively, from the values consistent with the binding energy). Had we taken the atomic calculation of McGuire to represent the shape, better agreement would have resulted. The enhancement was set at 7% at 70 eV. We choose $a=0.25 \text{ \AA}$ and $\mu=0.3 \text{ \AA}^{-1}$. As with Al and Si, except for a region of about 5 eV above the $L_{II,III}$ threshold, the fine structure is accounted for by the Shiraiwa modulation.

In aluminum our model predicts the correct overall spectral shape including structure at 83, 97, 112, and 128 eV, as well as a broad weak bump at about 160 eV. In silicon we can again account for the overall spectral shape but our predicted peaks at 132 and 158 eV occur about 6 eV higher than in the experiment. In sodium we predict structure at 37, 52, 62, and 86 eV in qualitative agreement with the synchrotron data.

In summary, we have shown that the structure above the $L_{II,III}$ soft x-ray absorption thresholds in Al, Si, and Na can be accounted for by the variation with energy of the transition matrix element, and a simple backscattering model to include the effect of the surrounding atoms. The greatest virtue of this approach is its simplicity: It allows the physical origin of observed structure to be readily assessed without recourse to a complete band-structure calculation.

In addition, the method appears to lend itself readily to improvements. The interaction between the outgoing electron and the core hole can be included easily, since a localized representation, appropriate for exciton effects, is being used. Stronger periodic fields can be included by considering multiple scattering from the surrounding ions. A more realistic pseudopotential should be used in computing the backscattering amplitude, and better core states should be used in the orthogonalization.

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Electronic Structure of GaAs†

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Using a nonlocal pseudopotential, including spin-orbit interactions, we have calculated a band structure for GaAs which is in excellent agreement with electroreflectance, wavelength-modulation, and photoemission experimental results. As in a calculation by Pandey and Phillips, an order of magnitude in accuracy has been gained over existing band structures; the largest discrepancy with Schottky-barrier electroreflectance measurements is less than 0.08 eV. The E_0' conflict is resolved in favor of Aspnes's interpretation.

The nonlocal pseudopotential approach has yielded what we believe to be the most accurate band structure for GaAs to date.¹ In fact, as a result of the extensive experimental studies on this compound, this band structure may be the most accurate band structure, over a large energy range, available for any material. The largest discrepancy between the experimental critical-point energies as determined by the Schottky-barrier electroreflectance of Aspnes and Studna² and as calculated by our nonlocal pseudopotential scheme is less than 0.08 eV. Further, we are able to achieve comparable agreement with the derivative reflectivity spectrum from wavelength-modulation measurements, and the electronic density of states as measured by photoemission experiments. This represents nearly an order-of-magnitude improvement over previous band-structure calculations. We are also able to confirm the existence of the critical points of Δ symmetry appearing in the E_0' structure, which lie about 10% of the way from Γ to X , in agreement

with the proposed assignment of Aspnes and Studna.² Spin-orbit interactions are found to be of prime importance in the formation of these critical points.

The band structure was calculated using the empirical pseudopotential method (EPM) which has been discussed extensively elsewhere.³ Since this method requires experimental information as input to fix the form factors, the recent experimental advances in electroreflectance techniques, in particular those developed by Aspnes,^{2,4} and high-resolution photoemission spectroscopy⁵ have proven to be quite valuable. According to Aspnes and Studna their electroreflectance measurements on GaAs have resulted in an order-of-magnitude improvement in the resolution and accuracy in the determination of critical-point energies as compared to previous spectroscopic work.² In addition, the advent of high-resolution photoemission spectroscopy has supplied us with detailed information on the lowest-lying valence bands in semiconductors. This information, in