L-shell ionization of surface atoms by backscattered electrons*

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Backscattering cross sections for the electron-impact L_1-shell ionization of Na, Mg, and S as well as the $L_{2,3}$-shell ionization of Mg, S, Cl, and Cu are reported. The use of target atoms chemisorbed on a metal surface allow measurement of the weak intensities in the backscattered region. The Burhop first Born approximation theory is shown to qualitatively describe the primary-electron energy dependence of these backscattering ionization cross sections. However, the theoretical cross sections are generally too low, particularly for the highest primary-electron energies studied.

I. INTRODUCTION

Until recently, cross-section measurements for electron-impact inner-shell ionization have been limited to the determination of total cross sections for K- and L-shell ionization of a few elements. Most of these measurements were made by studying the efficiency of excitation of characteristic x radiation resulting from the filling of the inner-shell vacancies introduced by electron impact. Using this method, relative values for the total cross section have been measured for the L_2- and L_3-shell ionization of Au,[1] for the L_1-, L_2-, and L_3-shell ionization of W,[2] and for the L_3-shell ionization of Ag.[3] Absolute total ionization cross sections for the three L shells of Au have been made more recently by Green,[4] Salem and Moreland,[5] and Davis, Mistry, and Quarles.[6]

Mehlhorn[7] recently showed that Auger electrons provide a method for determining the inner-shell ionization cross sections of low-atomic-number gas atoms. Cross sections for the K shells of C, N, O, and Ne[7] and for the $L_{2,3}$ shell of Ar[8] were measured by Mehlhorn and co-workers. More recently, the authors[9,10] used the Auger technique in conjunction with single atomic layers adsorbed on a metal surface to measure the K- and L-shell total ionization cross sections of various elements.

Theoretical study of inner-shell ionization has mainly been concerned with K-shell ionization where the experimental emphasis has been placed. Theoretical description of L-shell ionization also poses more problems, at least in obtaining analytical solutions for inelastic scattering cross sections. Burhop,[11,12] however, has presented one solution to this more complicated problem by use of the first Born approximation to obtain cross-section expressions for ionization of the three L shells of isolated atoms. He compared this theory with some of the relative experimental[1,13] values of total cross section for the L shells of Ag and Au

then available. The relative comparison between theory and experiment was surprisingly good at intermediate energies (7–10 times the ionization energy). The theory exceeded the measurements substantially in the higher-energy regime, due partially to relativistic effects which were not considered. Total-cross-section measurements of the $L_{2,3}$-shell ionization of the lower-atomic-number elements S, Cl, Ti, and Cu were performed by the authors.[10] They show agreement within a factor of 2 with the Burhop theory from 1.5 to 5 times the ionization energy. However, the Burhop theory for L-shell ionization has not been compared with angularly dependent experimental data.

Recently, we described[14,15] a new technique to determine cross sections for inner-shell ionization which are differential in energy and are integrated over 128° to 148° backscattering angle. These cross sections were obtained by electron-impact K-shell ionization of a single adlayer of atoms on a metal surface. In this surface technique, large numbers of atoms (~10^{13}) are involved in the scattering, resulting in detectable currents even in the low-intensity backscattered region. The bound electrons in the surface atoms are scattered to unfilled states within a 3-eV energy range above the Fermi level. The backscattered primary electrons identify this excitation or ionization mechanism from their discrete energy loss. The number of backscattered electrons with this loss energy is directly proportional to the backscattering ionization cross section.[15]

The backscattering cross sections obtained for K-shell ionization of C, N, O, and Na were found to be an interesting test of the Burhop theory. The measured and calculated cross sections both decrease with increased atomic number and with primary energy. However, the computed cross sections were found to be 10 to 300 times less than the experimental cross sections over the energy

ranges studied. The disagreement *increased* with energy rather than decreased, as in the total-cross section comparisons.[9,10]

In this paper we extend the backscattering ionization measurements and comparisons with the Burhop theory to the L_1 and $L_{2,3}$ shells.

II. APPARATUS AND PROCEDURE

The apparatus and backscattering ionization cross-section measurement technique were recently described in detail by the authors.[14,15] Briefly, the surface is bombarded by a normally incident monoenergetic beam of electrons. The secondary electrons are energy analyzed by a two-stage retarding-field–cylindrical-mirror analyzer. Separation of constant-energy-loss features in the secondary-electron energy distribution is accomplished by sweeping the electron-gun energy while maintaining fixed analyzer band-pass energy. The resulting energy-loss spectrum is double differentiated with respect to secondary-electron energy in order to accent the ionization step features with respect to the smooth secondary electron background. The ionization cross sections, differential in energy and integrated over 20° of backscattering angle, are then proportional to the amplitudes of the ionization loss features.

Energy-loss spectra for Na, Mg, S, Cl, and Cu adsorbed independently on W(100) are shown in Fig. 1. S and Cl were adsorbed on clean W(100) at ~100 °C as H_2S and CCl_4. Na was evaporated from a Pyrex ampoule,[16] Mg from a W wire, and Cu from an alumina crucible. The saturated coverages of Na,[16] S, and Cl on W(100) at ~100 °C were assumed to be one atomic monolayer. The coverages of Mg and Cu were assumed to be one monolayer when their Auger peak intensities were 0.25 that asymptotically obtained with many monolayers.[17] These coverages are believed to be accurate within a factor of 2, except for Na which is accurate to ±20%.[16]

The second minimum and maximum for the $S(L_{2,3})$ or $Cl(L_{2,3})$ spectrum in Fig. 1 may correspond to a second step in the density of states at the vacuum level.[18] Only the low-energy minimum and maximum are employed in these measurements of differential cross section. The $L_{2,3}$-shell ionization energies of Mg, S, and Cl are too close together (<2 eV) to be resolved in these experiments. The $Cu(L_{2,3})$ levels were resolved, however, and their corresponding ionization cross sections were added together for comparison with the other totaled $L_{2,3}$-shell cross sections.

The ionization spectra for $Na(L_1)$, $Mg(L_1)$, and $Mg(L_{2,3})$ in Fig. 1 were obtained at higher resolution (1.5-eV analyzer resolution and 0.75-eV rms

band-pass oscillation) than the others. This resolution was employed to measure the cross-section-vs-energy curves. For the absolute-cross-section determination, all results were normalized to the same 3-eV analyzer resolution and 2-eV band-pass oscillation values.

It was shown in a previous paper[15] that the current I_i contained within band-pass energy width (3 eV) of an ionization step edge is

$$I_i = \beta(Y_i/Y_p)I_p, \qquad (2.1)$$

where Y_p and Y_i are the intensities of the first minimum of an arbitrary double differentiated elastic peak and ionization step, respectively, and I_p is the current in that elastic peak. The constant β was found from numerical simulations to be 1.2, provided the ionization feature has no significant natural broadening and is steplike in shape. The $Na(L_1)$, $S(L_1)$, $S(L_{2,3})$ $Cl(L_{2,3})$, and $Cu(L_{2,3})$ ionization spectra have the characteristic shape of double-differentiated steps.[15] The β values of 1.2 to 1.7 were used for these spectra, depending on the amount of natural step broadening found. The $Mg(L_1)$ and $Mg(L_{2,3})$ spectra are more peaklike in shape; so β values of 1.2 and 1.0 were employed for them, respectively, the 1.2 value
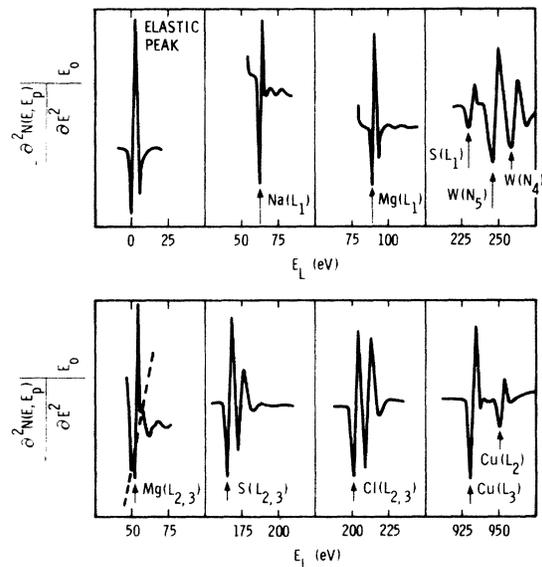

FIG. 1. Double-differentiated elastic peak and L-shell ionization loss spectra for various elements adsorbed independently on W(100). Energy loss $E_L = E_p - E$, where E_p and E are primary- and secondary-electron energies, respectively. Energy loss is arbitrarily measured with respect to the low-energy-loss minimum of the double-differentiated elastic peak. The primary energy and gain used to obtain each curve are different; the relative magnitudes of the ionization peaks are contained in Figs. 2 and 3.

accounting from some broadening. The $Mg(L_{2,3})$ spectrum is on a steep, sloping background indicated by the dotted line in Fig. 1. This background was subtracted out for the cross-section measurements.

The total error in these absolute-cross-section measurements, including errors in analyzer transmission, coverage, and the numerical simulations of double differentiation, is about a factor of 3. Allowing for changes in analyzer transmission and resolution with energy, the shapes of the cross-section-vs-energy curves are accurate to within 50% from one end to the other. If anything, the cross sections are low at high energy owing to the slight reduction of resolution and transmission with energy.

III. COMPARISON OF BACKSCATTERING CROSS SECTIONS WITH THEORY

Burhop[11,12] has formulated a first Born approximation theory for the electron-impact ionization of L shells of isolated atoms. In this formulation, a plane wave is used to describe the incident electron and a spherical wave represents the scattered primary electron. The initial and final states of the ejected core electron are described respectively by a hydrogenic wave function and a Coulomb wave function. Using this simple description, the general expression for the differential cross section for L-shell ionization is found to be[11,12]

$$I(K,\kappa)dK\,d\kappa = \frac{2^{14}\pi\,\mu^6\kappa[\mu^4 + 2(K^2+\kappa^2)\mu^2 + (K^2-\kappa^2)^2]^{-5}A}{15a_0^2k^2[1 - \exp(-4\pi\mu/\kappa)]}$$

$$\times \exp\left[-\frac{4\mu}{\kappa}\arctan\left(\frac{2\mu\kappa}{K^2-\kappa^2+\mu^2}\right)\right]dK\,d\kappa,$$
(3.1)

where $\mu = (z-2)/a_0$ with a_0 as the Bohr radius. The initial and final momenta of the incident electron k and k' are related to the momentum of the ejected electron, κ, and the ionization energy E_i by the energy equation

$$(\hbar^2/2m)(k^2 - k'^2) = E_i + \hbar^2\kappa^2/2m.$$
(3.2)

The factor A determines the L-shell wave function being studied. For $2s$,

$$A_{2s} = 20\mu^{10} + \mu^8(85\kappa^2 + 47K^2) + \mu^6(140\kappa^4 + 100K^4)$$

$$+ \mu^4(110\kappa^6 - 82\kappa^4K^2 - 310\kappa^2K^4 + 410K^6)$$

$$+ 40\mu^2(\kappa^2 - K^2)^2(\kappa^4 + \kappa^2K^2 - 4K^4)$$

$$+ 5(\kappa^2 - K^2)^4(\kappa^2 + 3K^2).$$
(3.3)

For $2p\,(m=0)$,

$$A_{2p0} = 23\mu^{10} + \mu^8(76\kappa^2 + 204K^2)$$

$$+ \mu^6(90\kappa^4 + 444\kappa^2K^2 + 218K^4)$$

$$+ 4\mu^4(\kappa^2 - K^2)(11\kappa^4 + 80\kappa^2K^2 + 85K^4)$$

$$+ \mu^2(\kappa^2 - K^2)^2(7\kappa^4 + 50\kappa^2K^2 + 135K^4).$$
(3.4)

For $2p\,(m=\pm1)$

$$A_{2p1} = 4\mu^4(4 + \kappa^2/\mu^2)(\mu^2 + \kappa^2 + 5K^2)$$

$$\times [\mu^4 + 2(K^2 + \kappa^2)\mu^2 + (K^2 - \kappa^2)^2].$$
(3.5)

[The factor $(4 + \kappa^2/\mu^2)$ in (3.5) was not included in Burhop's original paper due to a typographical error.[12] It should be noted that calculations by the authors in a previous paper[19] which did not include this factor led to calculated cross sections approximately 3 times too small for the $L_{2,3}$ ionization of Mg, Cl, and Cu. Also, a 3-eV spread in the ejected energy is employed here as it is a more accurate description of the analyzer resolution than the 2-eV value used in Ref. 19. The calculated values for $L_{2,3}$ ionization cross section given here therefore range from 4 to 10 times the values given for Mg, Cl, and Cu in Ref. 19.] For the consideration of L_1-shell ionization,

$$A = 2A_{2s}.$$
(3.6)

In the $L_{2,3}$-shell investigation,

$$A = 2A_{2p0} + 4A_{2p1}.$$
(3.7)

In order to compare with backscattering experimental data, we used the momentum-transfer definition to obtain the angular dependence:

$$K = |\vec{k} - \vec{k}'| = (k^2 + k'^2 - 2kk'\cos\theta)^{1/2}.$$
(3.8)

The analyzer defines the upper limit of the integration on the ejected electron momentum to conform with an energy spread of 3 eV above the Fermi level (7.5 eV) of the W substrate. The 128° to 148° backscattering accepted by the analyzer defines the limits of integration on θ.

Backscattering cross sections $\Delta\sigma$ for the L_1-shell ionization of Na, Mg, and S adsorbed on W(100) are shown in Fig. 2 as a function of reduced primary energy. Corresponding cross sections for the $L_{2,3}$-shell ionization of Mg, S, Cl, and Cu are displayed in Fig. 3. The experimental values, depicted by the solid lines, are compared with calculated backscattering cross sections (dashed lines) obtained from the Burhop theory.

The L-shell calculations show the experimental trend of reduced backscattering cross section with increased primary-electron energy and increased atomic number. The theory, however, is too steep a function of energy except possibly for $Cu(L_{2,3})$. In addition, the theory is at least

an order of magnitude low for $X = 4.0$ in the cases of the L_1 shell. The theory is without doubt low for $X = 4.0$ in the cases of the $L_{2,3}$ shell as well.

IV. COMMENTS AND CONCLUSIONS

As stated earlier, measurements of the K-shell backscattering ionization cross sections of C, N, O, and Na were found[15] to be 1 to $2\frac{1}{2}$ orders higher than the Burhop theory. We see in this work that there is better agreement between L-shell backscattering cross sections and the Burhop theory. In fact the agreement seems to increase with increased principal and angular-momentum quantum numbers; i.e., agreement is least for the K shell and best for the $L_{2,3}$ shell. The experimental measurements for a given ionization energy do not change so much from shell to shell as do the Burhop calculations; i.e., the theoretical cross-section-vs-reduced-energy curves become less steep in the sequence K, L_1 to $L_{2,3}$ shell.

In view of the disagreement noted between the experimental differential cross sections and those calculated from the one-event theory, additional possibilities for the actual kinematics of L-shell ionization of surface atoms must be considered. Double scattering involving elastic reflection by the W(100) substrate plus forward inelastic scattering by the overlayer, or vice versa, is also a possible mechanism.

A good estimate[15] of the cross section for this double scattering is

$$\Delta\sigma_{ds}(E_p) \approx \rho\sigma_F(E_p)[R_A(E_p) + R_A(E_p - E_i)], \quad (4.1)$$

where

$$\sigma_{fs}(E_p) = \int_F \sigma(E_p, \hat{k}, \hat{k}')d\Omega', \quad (4.2)$$
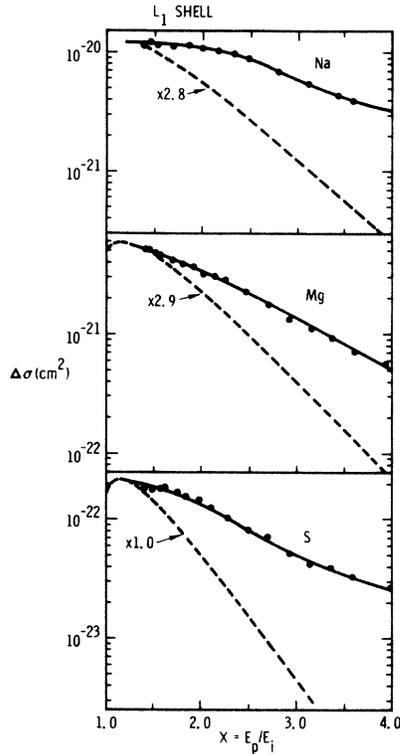

FIG. 2. Backscattering cross sections $\Delta\sigma$ for L_1-shell ionization of Na, Mg, and S adsorbed on W(100). The solid lines are fits of the experimental points. The dashed lines are cross sections computed from the Burhop first Born approximation theory for L_1-shell ionization. These theoretical curves are multiplied by the constants, as indicated, to be tangent to the experimental curves.
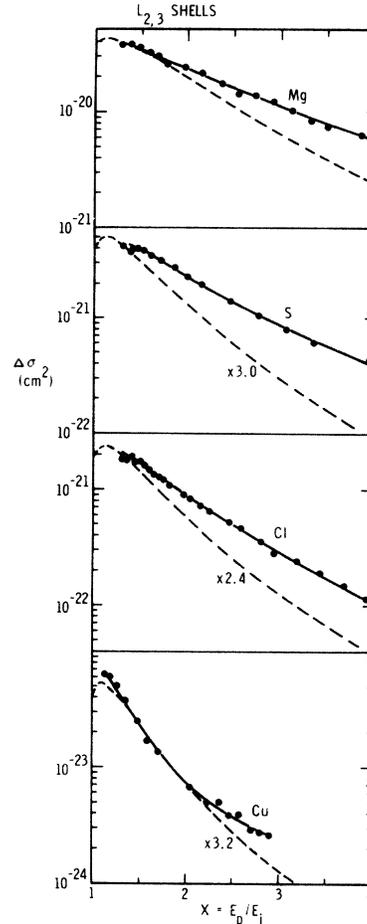

FIG. 3. Backscattering cross sections $\Delta\sigma$ for $L_{2,3}$-shell ionization of Mg, S, Cl, and Cu adsorbed on W(100). The solid lines are fits of the experimental data and the dashed lines are computed from the Burhop theory. The theoretical curves are magnified, as indicated, to be tangent to the experimental curves.

with E_p and E_i, respectively, the primary-electron and L-shell ionization energies. R_A is the ratio of the elastic current accepted by the analyzer aperture divided by the primary-electron current. ρ is the absorption factor (=0.75) for the overlayer. The cross section σ_F represents the forward ionization scattering computed from the theory discussed in Sec. III. The integration over the solid angle Ω' of the scattered-electron momentum vector $\hat{k}'$ was carried out for angles of 0° to 20° between incident and scattered momentum directions. Since the Burhop theory gives good agreement with total-cross-section data, such calculations are a reasonable estimate of the inelastic scattering into the forward direction.

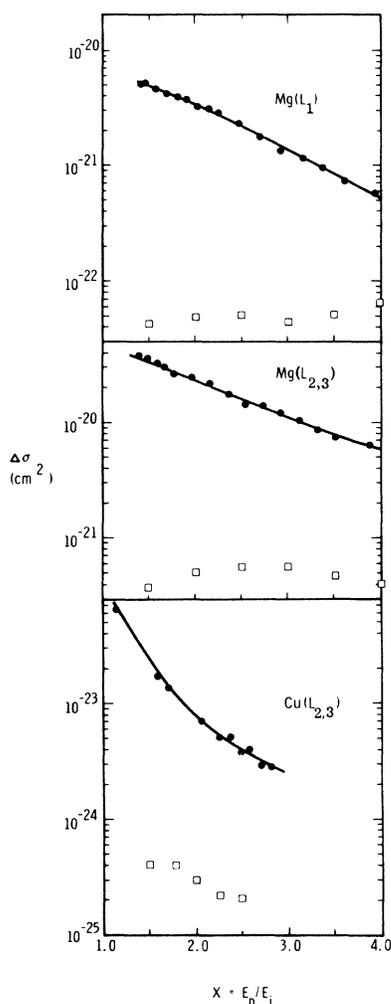Figure 4 shows estimates of the double-scatter-

FIG. 4. Computed double scattering (squares) compared with the experimental ionization cross sections (dots and solid lines) for Mg(L_1), Mg($L_{2,3}$) and Cu($L_{2,3}$).

ing contributions (squares) computed from (4.1) for Mg(L_1), Mg($L_{2,3}$), and Cu($L_{2,3}$). These cross sections for double scattering are compared with the experimental cross sections (solid lines) for the corresponding ionizations. The double scattering is seen to be negligible at low energies and is an order of magnitude below the experimental curve at the highest energies studied. Double scattering therefore is not likely to account for the differences between the calculations based on the one-event theory and the experimental differential cross sections, particularly for the L_1 shell.

In our use of the Burhop theory, we assume that the ejected core electrons are free-electron-like in energy behavior. The energy dependence of the ejected electrons is thereby governed by (3.2). Although this energy dependence is more complicated when the band-structure[15] term is included, the actual effect on backscattering cross-section determination is small. This is borne out by the fact that undifferentiated energy-loss curves corresponding to Fig. 1 demonstrate very little threshold structure, except in the case of Mg, where it could contribute a factor of 2. But the large differences between the Burhop theory and the L_1-shell experimental cross sections clearly cannot be explained by density-of-states effects.

The inadequacy of the Burhop first Born approximation theory for the description of K- and L-shell backscattering ionization is thus apparent. This inadequacy most likely can be attributed to the assumed plane-wave description of the incident and scattered primary electrons, which is inherent to the first Born approximation. In reality, Coulomb forces between the nucleus and the incident and scattered waves act to strongly distort those waves. Shelton *et al.*[20, 21] have shown that a distorted-wave treatment of the excitation of hydrogen and helium substantially increases (by orders of magnitude) the cross sections for backscattering compared with the first Born approximation description. Although this L-shell study and the previous K-shell study differ somewhat from this type excitation, a more realistic wave-function description for the incident and scattered electrons should improve the prediction of K- and L-shell backscattering ionization. Larger cross sections, especially at low energies, can also be expected if exchange[20] contributions are included.

In conclusion, the comparison of new backscattering cross-section data for L-shell ionization with the Burhop ionization theory shows the inadequacy of the theory in the backscattered region. Previous total-cross-section data do not demonstrate this deficiency since in total-cross-section calculations forward-scattering contributions predominate.

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