PHYSICAL REVIEW VOLUME 170, NUMBER 1 5 JUNE 1968

Double Electron Ejection in the Photoabsorption Process[*]

MANFRED O. KRAUSE, THOMAS A. CARLSON, AND R. D. DISMUKES[†]
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 15 January 1968)

Electrons ejected from neon by Mg K_α and Al K_α x rays and from argon by Ti K_α x rays have been studied with an electrostatic energy analyzer. On the low-energy side of the photolines characteristic of single electron emission, discrete peaks and continua are observed which respectively indicate excitation and ionization of a second electron. From these electron spectra, the following probabilities of two-electron transitions are derived (per photoabsorption event): Ne KL: $(18.5\pm1.0)\%$; Ar KL: $(2.5\pm0.8)\%$; and Ar KM: $(20.7\pm1.4)\%$. In about 85% of the double events, both electrons go into the continuum; in about 15%, the less tightly bound electron is promoted to excited discrete states. With the use of single-electron Hartree-Fock wave functions, the theory of electron shakeoff accounts for the observed intensities. The shape of the continuum electron spectra is in fair agreement with theoretical predictions. About 80% of the shakeoff electrons have energies of $0\leq E\leq E_i$, where E_i is the binding energy of the L or M electron in an atom that lacks one K electron. Consequences of the present study in regard to x-ray and Auger-electron satellites are discussed, and it is found that specific satellites can be associated with specific double-hole configurations. The following relative intensities of K_α satellites were measured for Mg, Al, and Ti: 13%, 8.5%, and 4%, respectively.

I. INTRODUCTION

FROM previous measurements[1–6] of charge states of ions formed following photo-ionization in an inner shell we concluded that more than one electron can be ejected in the photoabsorption process. In the most amenable case of x rays interacting with neon atoms we found KL and KLL ionization to occur, respectively, in 16% and 1.5% of the events.[1,3] Neither the energy distribution of the emitted electrons nor events of ionization of a K electron and simultaneous *excitation* of an L electron could be observed in this type of experiment. All these quantities are, however, important if the experimental observations are to be related to theory. In the present study we have analyzed electrons emitted in the photoabsorption process, and by this method have been able to determine directly (a) the probability of double ionization, (b) the probability of simultaneously ejecting one electron and promoting another to an excited discrete level, and (c) the energy spectra of the continuum electrons. We bombarded neon with Mg K_α and Al K_α x rays, and argon with Ti K_α x rays, and studied those electrons that originated from the K, KL, and KM shells. Experimental observations will be described in Sec. II.

As we have done previously[1–6] we employed the sudden-approximation or shakeoff theory[7] to interpret the results. This theory attributes the emission of a second[8] electron to the sudden perturbation of the atomic potential at the moment of the departure of the first electron. We therefore regard double photo-ionization as proceeding in two stages: first, photo-ionization proper, and second, excitation of another electron by the change in screening together with the relaxation of the remaining electrons from orbitals of the neutral atom to orbitals of the ionized atom. This approach neglects other mechanisms that may lead to two-electron transitions, such as interchannel interactions and correlation effects in the ground (initial) state. Since the latter mechanisms appear to contribute little to the processes reported here we can adopt the following terminology without prejudicing cases in which the shakeoff process accounts only for part of the double photo-ionization events: "photoelectron" is the electron emitted in single electron transitions; "shakeoff electron" refers to the slower electron, and "complementary shakeoff electron" to the faster electron of a simultaneously excited pair in two-electron transitions.

The calculation procedure of the theory will be outlined in Sec. III, and in Sec. IV we show that the electron-shakeoff concept provides a quantitative description of the results of this paper and related data such as x-ray and Auger-electron satellites and distributions of ion charges following photo-ionization or β decay.

A brief historical note will serve to point out the relation of the present investigation to other areas of atomic physics. Double-electron excitation was held responsible for the occurrence of K x-ray satellites[9] as early as 1921. Although these satellites were thought originally to appear only under electron bombardment,[10]

---

[*] Research sponsored in part by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[†] U. S. Atomic Energy Commission Health Physics Fellow, Vanderbilt University, Nashville, Tenn.

[1] M. O. Krause, M. L. Vestal, W. H. Johnston, and T. A. Carlson, Phys. Rev. **133**, A385 (1964).

[2] T. A. Carlson and M. O. Krause, Phys. Rev. **137**, A1655 (1965).

[3] T. A. Carlson and M. O. Krause, Phys. Rev. **140**, A1057 (1965).

[4] M. O. Krause and T. A. Carlson, Phys. Rev. **149**, 52 (1966).

[5] T. A. Carlson, W. E. Hunt, and M. O. Krause, Phys. Rev. **151**, 41 (1966).

[6] M. O. Krause and T. A. Carlson, Phys. Rev. **158**, 18 (1967).

[7] J. S. Levinger, Phys. Rev. **90**, 11 (1953); see also Ref. 3 for further citations.

[8] Unless specifically needed, we will always speak of a "second" electron (or double electron emission) although there is a finite probability of expelling a third, fourth, etc. electron.

[9] G. Wentzel, Ann. Physik **66**, 437 (1921); see also M. J. Druyvesteyn, Z. Physik **43**, 707 (1927); F. Bloch, Phys. Rev. **48**, 187 (1935).

[10] A. E. Sandström, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXX, p. 85.

it was shown[11] in 1964 that they occur also in fluorescence. Two extensive theoretical treatments based on the sudden approximation have recently been advanced[12,13] and have proven successful in accounting for the observed satellite intensities. The occurrence of Auger-electron satellites, the pendants to x-ray satellites, was demonstrated by Körber and Mehlhorn[14] in 1966. Besides satellite lines due to initial double-hole configurations, electron shakeoff concomitant to β decay has perhaps the closest relationship to the present work; the effects arise from the same cause—a sudden perturbation of the atomic potential. Several experimental[15,16] and theoretical[7] papers of the past ten years report on the emission of orbital electrons together with the β particle.

A large body of further information on two-electron excitation and ionization processes has recently been gathered. We cite the following: (1) simultaneous excitation of a K and L electron of argon[17] exhibited in the photoabsorption curve, (2) excitation and ionization of outer electrons in rare gases by photon[18–20] and electron[21] impact, (3) yield of auto-ionization electrons from He under proton[22] and electron[23] bombardment, (4) breaks in ionization efficiency curves[24] of ions produced by electron impact, and (5) two electron emission[25] in Auger processes.

Some of the studies listed in this brief review have been or possibly will be interpreted with the aid of the shakeoff principle; others appear to require a more sophisticated theoretical approach, e.g., the inclusion of electron-correlation effects in the matrix elements of the transition rates.[19,20,25]

II. EXPERIMENT

The apparatus has been described earlier.[26] The experimental procedure was as follows: x rays from Mg, Al, and Ti anodes entered the gas chamber through a thin Be window, 0.0025 cm thick for Mg and Al, and 0.03 cm thick for Ti radiation. Electrons expelled perpendicular to the x-ray beam were energy-separated by an electrostatic analyzer and detected individually by an open electron multiplier Du Mond SP172. Data were acquired automatically: Electrons were sorted according to their energies by applying a dc-biased sawtooth voltage to the analyzer plates, and signals were stored in the memory of a pulse-height analyzer whose channel advance was synchronized with the voltage sweep. Minimizing fluctuations of x-ray flux and gas pressure by this mode of operation was essential for the long times necessary for data acquisition. Synchronization, voltage waveforms, and bias voltages were sufficiently stable so that no shift in peak position or line broadening occurred. Multiplier response to electrons of different energies was checked with the aid of an electron gun and found to vary only slowly ($<10\%$) over the energy ranges of interest. Transmission of the instrument proved essentially independent of energy, as tested with a thermionic electron source. Gas pressures were of the order of 10^{-2} Torr in the gas cell and less than 5×10^{-5} Torr in the analyzer and detector section.

Observed electron energy spectra needed to be corrected for the dispersion of the instrument, variation of multiplier response, and background consisting of detector noise and photoelectrons from the bremsstrahlung continuum. The latter correction was small and constant over the spectra as judged from regions where only bremsstrahlung would contribute. The most important correction to the data was for inelastic energy losses suffered by the photoelectrons on their way from the source to the analyzer in collisions with neutral gas atoms. In auxiliary runs we produced thermionic electrons in the source volume and recorded magnitude and spectral shape of the inelastic losses under the conditions of the x-ray experiment. Photopeak and peak of unscattered electrons of the same energy were then matched and the loss spectrum was subtracted from the x-ray-induced spectrum. In some cases (see Fig. 1), when the inelastic peak of the loss spectrum was resolved from the unscattered peak or photoline, the loss spectrum itself could be matched at the inelastic peak. Reliability of the procedure was ascertained by repeating the experiment at different pressures.

In Fig. 1 we present the energy spectrum of electrons expelled from neon atoms by 1.25-keV Mg K_α x rays.

---

[11] R. D. Deslattes, Phys. Rev. **133**, A399 (1964).

[12] V. P. Sachenko and V. F. Demekhin, Zh. Eksperim. i Teor. Fiz. **49**, 765 (1965) [English transl.: Soviet Phys.—JETP **22**, 532 (1966)].

[13] T. Åberg, Phys. Rev. **156**, 35 (1967).

[14] H. Körber and W. Mehlhorn, Z. Physik **191**, 217 (1966). The lines were excited by electron bombardment; unpublished data of the present authors taken with poorer resolution indicate the presence of the same lines and similar intensities under x irradiation.

[15] A. H. Snell and F. Pleasonton, Phys. Rev. **111**, 1338 (1958); T. A. Carlson, *ibid.* **131**, 676 (1963); N. L. Lark and M. L. Perlman, *ibid.* **120**, 536 (1960).

[16] F. Suzor, J. Phys. Radium **21**, 223 (1960); E. E. Berlovich, L. M. Kutsentov, and V. G. Fleischer, Zh. Eksperim. i Teor. Fiz. **48**, 1013 (1965) [English transl.: Soviet Phys.—JETP **21**, 675 (1965)].

[17] Ch. Bonnelle and F. Wuilleumier, Compt. Rend. **256**, 5106 (1963); H. W. Schnopper, Phys. Rev. **131**, 2558 (1963).

[18] R. P. Madden and K. Codling, Astrophys. J. **141**, 364 (1965).

[19] T. A. Carlson, Phys. Rev. **156**, 142 (1967).

[20] F. W. Byron and C. J. Joachain, Phys. Letters **24A**, 616 (1967); Phys. Rev. **164**, 1 (1967).

[21] B. L. Schram, A. J. H. Boerboom, and J. Kistemaker, Physica **32**, 185 (1966); W. Bleakney and P. T. Smith, Phys. Rev. **49**, 402 (1936); M. J. Van Der Wiel, F. J. DeHeer, and G. Wiebes, Phys. Letters **24A**, 423 (1967); F. Fiquet-Fayard, J. Chem. Phys. **62**, 1065 (1965).

[22] M. E. Rudd, Phys. Rev. Letters **15**, 580 (1965).

[23] W. Mehlhorn, Phys. Letters **21**, 155 (1966).

[24] J. P. Ziesel, J. Chem. Phys. **62**, 328 (1965).

[25] T. A. Carlson and M. O. Krause, Phys. Rev. Letters **14**, A543 (1965); **17**, 1079 (1966); M. Wolfsberg and M. L. Perlman, Phys. Rev. **99**, 1833 (1955). Satellite lines in Auger spectra of K and Cl [A. Fahlman, K. Hamrin, G. Axelson, C. Nordling, and K. Siegbahn, Z. Physik **192**, 484 (1966)] probably indicate excitation of a second electron in an Auger process.

[26] M. O. Krause, Phys. Rev. **140**, A1845 (1965); Phys. Letters **19**, 14 (1965).

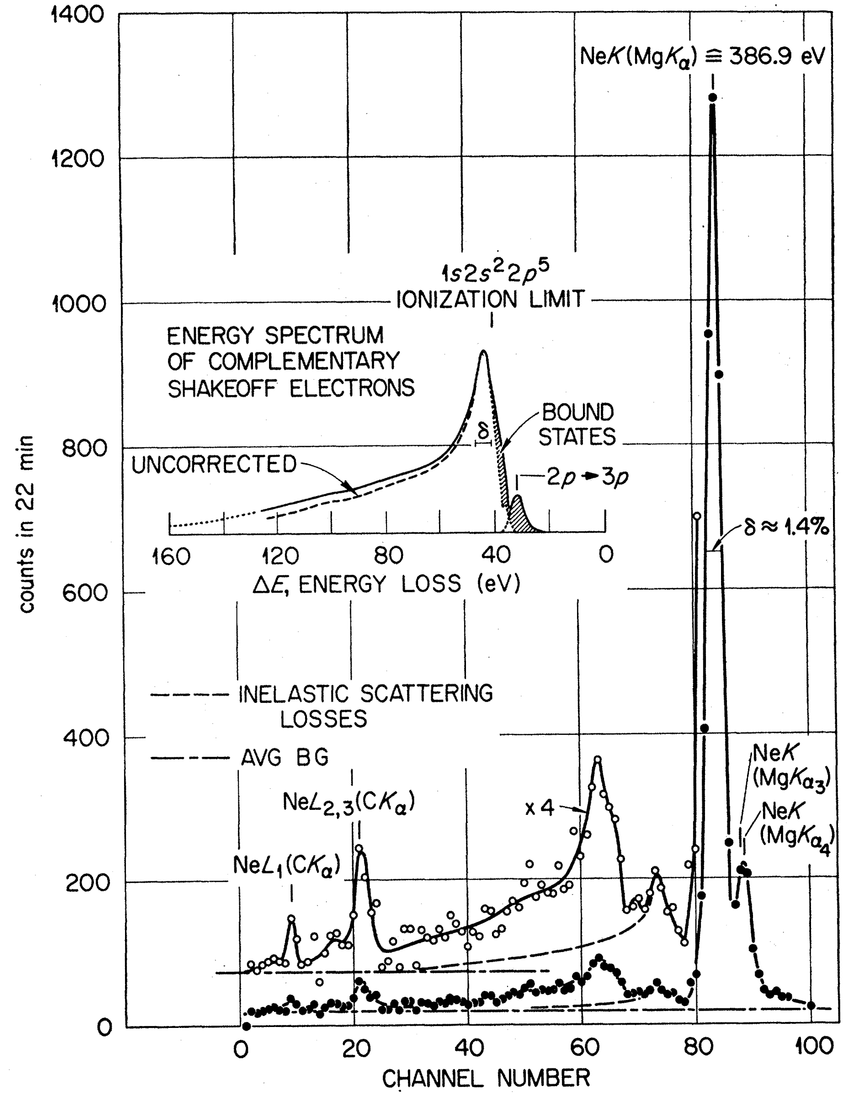

Fig. 1. Energy spectrum of electrons ejected form neon by Mg K_α x rays. Photoline Ne $K(\mathrm{Mg}K_\alpha)$ indicates single-electron emission; continuous distribution indicates emission of K and L electron. Inset figure (dashed line) is obtained from recorded spectrum after subtraction of inelastic scattering losses and background. Solid contour represents fully corrected spectrum. Channel numbers are substituted in insets of this and following figures by energy scale whose origin is at location of photopeak.

This spectrum, as well as those of the following figures, is uncorrected and representative of at least three individual observations. The line at 387 eV corresponds to the emission of a single electron in the common photoelectric effect

$$E=h\nu-E_K, \tag{1}$$

where $h\nu$ is the photon energy and E_K the binding energy of the neon K electron. The weak peak on the high-energy side of the photoline is due to Mg K_α satellite lines, whereas the rise near channel 72 is produced by photoelectrons Ne $K(\mathrm{Mg}\ K_\alpha)$ that have lost energy in collisions with neutral neon atoms. The adjacent structure below channel 70 is attributed to a process in which a $2p$ electron, and to a lesser degree a $2s$ or several L electrons are excited or ionized in addition to a K electron. This follows from the energy balance for two-electron transitions:

$$\text{for excitation:}\quad E_1=h\nu-E_K-E_{2p(K)}^*, \tag{2}$$

$$\text{for ionization:}\quad E_1+E_2=h\nu-E_K-E_{2p(K)}=\text{const}, \tag{3}$$

where E_1 and E_2 are the kinetic energies of the ejected electrons, and $E_{2p(K)}^*$ and $E_{2p(K)}$ are the excitation and ionization energies of a $2p$ electron in a neon atom lacking one K electron. In this experiment we did not observe the energy distribution $f(E_2)$ of the slower electron which we designate as the shakeoff electron, but the distribution $f(E_1)$ of the so-called complementary shakeoff electron.[27] According to Eq. (3) one distribution is the mirror image of the other.

The energy distribution $f(E_1)$ is shown in the inset of Fig. 1 and evolves from the recorded distribution follow-

---

[27] Several workers (see Ref. 16) have measured the distributions $f(E_2)$ of shakeoff electrons that are released in β decay.

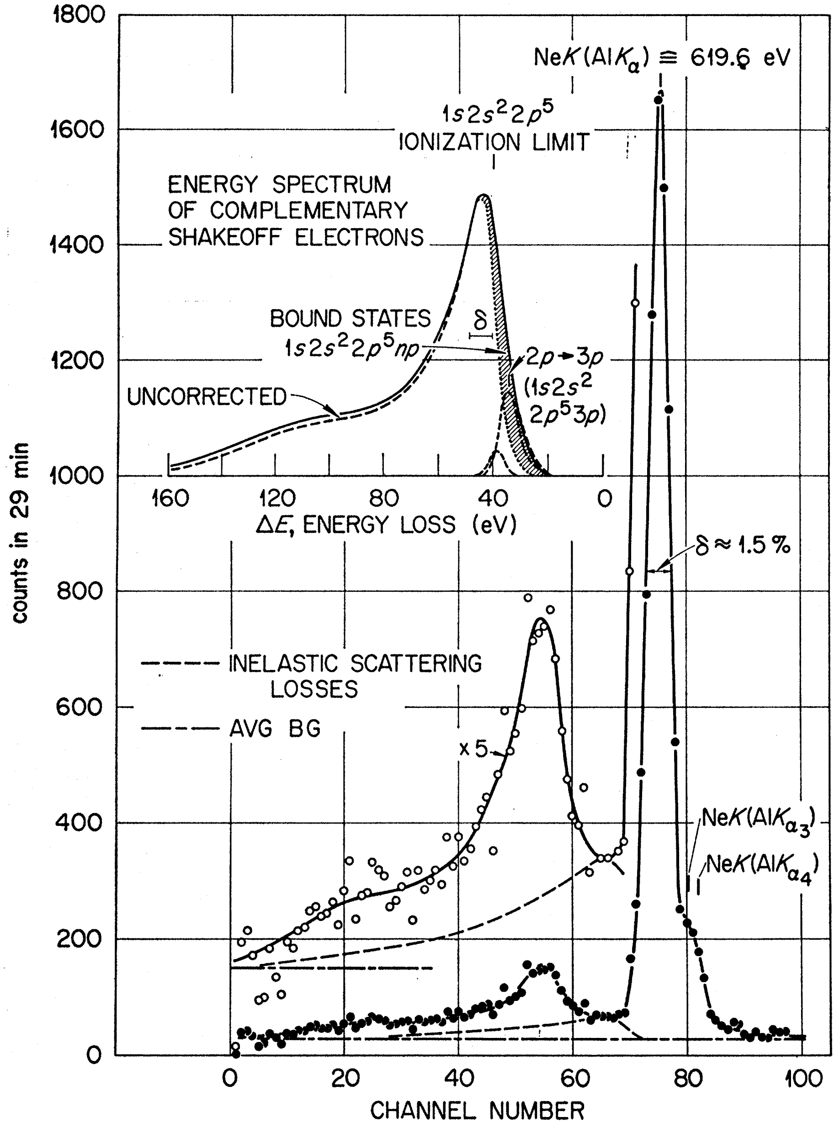

FIG. 2. Photoelectron peak Ne K(AlK_α) and continuous distribution due to shakeoff of L electrons concomitant to ejection of K electron.

ing subtraction of background and inelastic loss spectrum. The inset figure shows also the small change in contour when corrections for dispersion of the instrument and multiplier response are applied (corrections are made relative to the photopeak). Separation of continuum and excited states, indicated by the dotted line, was made on the basis of the following assumptions: First, in accordance with the hydrogenic law $I_n \propto n_{\mathrm{eff}}^{-3}$, the combined intensity of the transitions $2p \rightarrow np$, $n \geq 4$, does not exceed the intensity of the transition $2p \rightarrow 3p$, which is given by the reproducible peak near $\Delta E = 32$ eV. Second, the distribution of continuum electrons with energies *close* to the ionization limit is similar to the theoretical prediction. Even a large deviation from the latter assumption would have a small influence on the slope of the leading edge of the continuum. Uncertainties of the analysis are included in the errors quoted below for ionization energies and intensities of transitions to discrete and continuum states.

In Fig. 2 we show the energy spectrum of electrons that are expelled by Al K_α x rays of 1.49-keV energy. The curves exhibit the same features as seen in Fig. 1 except that with the same resolution less detail can be discerned at the higher electron energies of this experiment. Analysis of the spectrum followed the outlined steps and to separate continuum and discrete states use was made of the preceding results.

The photoline of Fig. 3 corresponds to the emission of a K electron from argon by Ti K_α x rays, and the continuous distribution (minus inelastic loss spectrum) is ascribed to the simultaneous loss of a K and an M electron. The spectrum was analyzed in the manner described above [substitute, for example, $E_{3p(K)}$ (Ar)

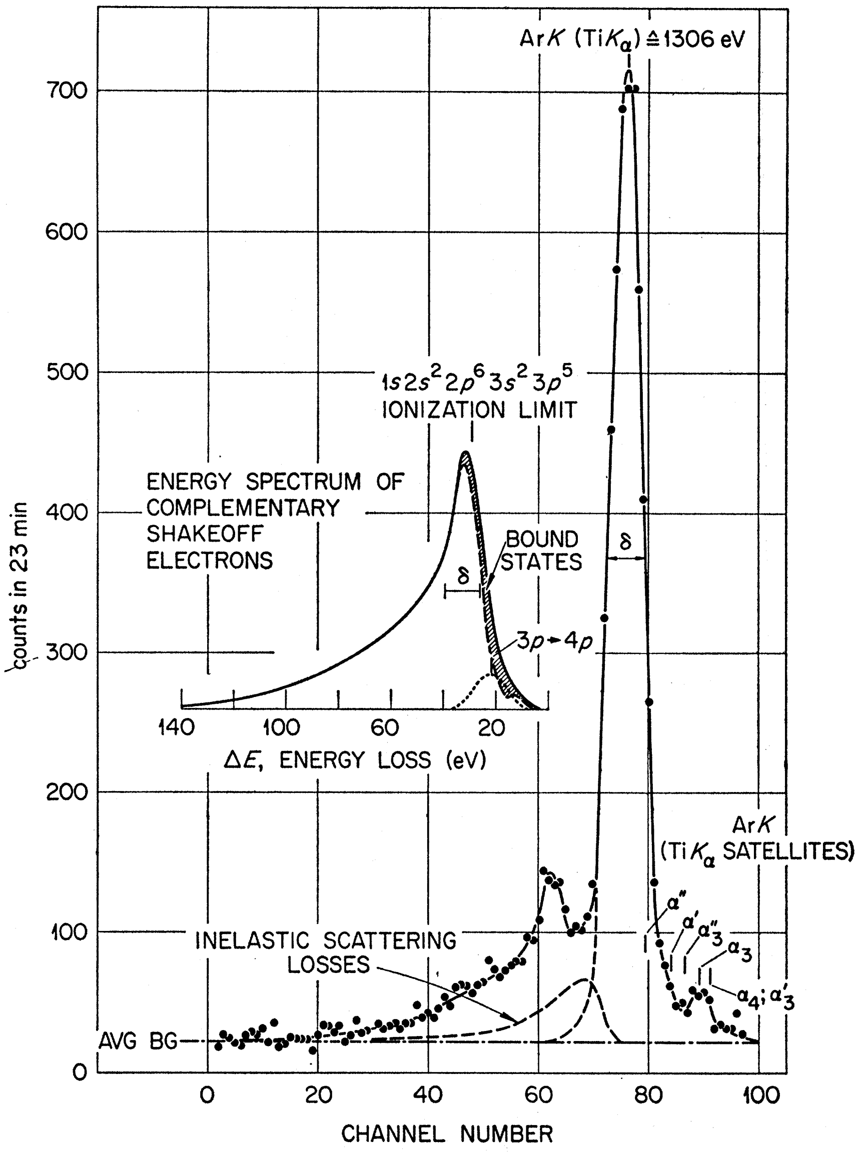

FIG. 3. Energy spectrum of electrons produced by the interaction of Ti K_α x rays with K and KM electrons of argon.

for $E_{2p(K)}$ (Ne) in Eq. (3)]. We note that here the background level is raised by a somewhat larger contribution from electrons ejected by bremsstrahlung quanta.

Ti K_α x rays possess sufficient energy to promote both a K and an L electron. The experimental spectrum arising from this interaction is shown in Fig. 4. Resolution was sacrificed to gain in intensity, and the energy scale (the sawtooth) was expanded at the expense of linearity over the entire range. Although statistics were poor for any individual run, the skewed peak arising at $\Delta E \approx 300$ eV was reproducible. Inelastic scattering losses were treated in the same manner as before and the rise in the inelastic loss spectrum near $\Delta E \approx 245$ eV and $\Delta E \approx 320$ eV gives evidence of the removal of a $2p$ or a $2s$ electron from a neutral argon atom. The "net" spectrum of the removal of an L electron together with a K electron is plotted in the inset in Fig. 4. Error bars include the statistical error and uncertainties in background, inelastic loss spectrum, and detector response.

III. THEORY

Before extracting results from the spectra of Figs. 1–4 we first touch on the theory of electron shakeoff.

The method of the sudden-approximation or electron-shakeoff theory[7] as it is usually called in this context appears to offer a simple way of calculating the probability of double-electron[8] promotion by a single photon.[28] It allows the use of single-electron wave

---

[28] Another approach is the use of the Born approximation whose high-energy limit is equivalent to the sudden approximation [J. M. Peek, Phys. Rev. **160**, 124 (1967)]. See also R. D. Richtmeyer, *ibid.* **49**, 1 (1936).

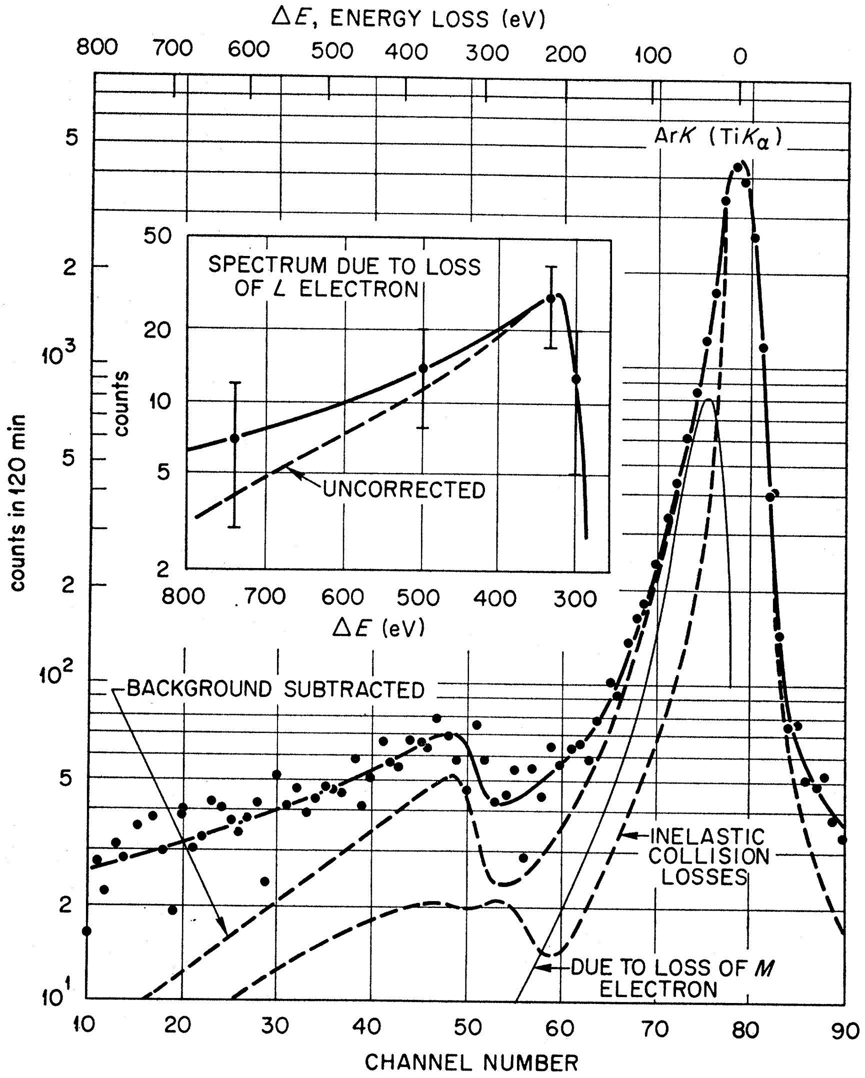

FIG. 4. Energy spectrum of electrons ejected from argon by Ti K_α x rays. Spectrum gives evidence of simultaneous emission of K and L electron. Also shown are distributions due to shakeoff of M electrons (thin line) and inelastic collision losses with neutral argon atoms (dashed line).

functions to describe the initial and final states of the system, and requires no reference to the "cause" of the change of potential whether it may be the creation of an inner hole by photon or particle impact, or the change of nuclear charge in β decay. It is also tacitly implied that the energy is conserved according to Eqs. (2) and (3). One condition must be met, however; that is, the change of potential must be sudden, specifically[3,13,29]:

$$(W_{nl,n'l'}-W_{nl})t_{n'l'}/\hbar\ll 1\,, \tag{4}$$

where W_{nl} is the energy of the initial state, $W_{nl,n'l'}$ the energy of the final state, and $t_{n'l'}$ is the time interval of the change in the Hamiltonian.

Transition probabilities are then given by

$$P=\left|\int\psi_{nl}(Z)\psi_{n'l'}^*(Z+\Delta Z)d\tau\right|^2, \tag{5}$$

where $\psi_{nl}(Z)$ and $\psi_{n'l'}^*(Z+\Delta Z)$ are the initial and final wave functions of the electron going from nl to $n'l'$, and ΔZ is the change in effective charge. If $n\neq n'$ (according to selection rules[7] l always equals l') transition probabilities $P_{n,n'}$ to excited states and continuum states are obtained; if $n=n'$ probabilities $P_{n,n}$ of the electrons remaining in their original orbitals are obtained. In the actual calculation, probabilities P_f of transitions to occupied states are also obtained so that the probability of no transition will be $P_n'=P_{n,n}+P_f$. Since good wave functions for continuum electrons are difficult to determine, one usually calculates $P_{n,n}$ and P_f the probability of vacating is then given by

$$P_v=1-P_n'\,. \tag{6}$$

It remains, therefore, uncertain whether the electron is excited or ionized. Assuming that transitions of the electrons available in a particular shell are stochastically independent, we get the probability $P_{n,r}^{(q)}$ of losing q

---

[29] This condition seems to be unduly severe; in the case of neon (Refs. 3 and 13) we found that it can be as large as 0.4.

electrons out of r electrons present in the n shell from

$$P_{n,r}{}^{(q)}=C_q{}^rP_v{}^q(1-P_v)^{r-q}, \tag{7}$$

where $C_q{}^r$ is the binomial coefficient.

Values reported in the following section have been computed with HF wave functions from the approximate expression

$$P_T=1-P_{n,n}{}^r-rP_f, \tag{8}$$

where P_T is the probability of removing any number of the r electrons present in the shell n, instead of the expression

$$P_T=1-(P_{n,n}+P_f)^r, \tag{9}$$

which introduces a negligible error, since P_f is ordinarily small as compared to $P_{n,n}$.

In one particular instance of the monopole transition $2p\rightarrow 3p$ in the neon atom lacking a $1s$ electron, we have calculated the transition probability directly. The initial state was then $\mathrm{Ne}^+\ 1s2s^22p^6$, and the two coupling schemes possible[30] yielded the following two final ^2S states:

$$\begin{aligned}{}^2S(\text{lower})=0.614\ &2p^53p(^3S)1s\ {}^2S\\ &-0.789\ 2p^53p(^1S)1s\ {}^2S,\end{aligned} \tag{10}$$

and

$$\begin{aligned}{}^2S(\text{upper})=0.734\ &2p^53p(^3S)1s\ {}^2S\\ &+0.679\ 2p^53p(^1S)1s\ {}^2S.\end{aligned} \tag{11}$$

Levinger[7] calculated direct transition probabilities with the aid of Eq. (5) and thus obtained energy distributions of shakeoff electrons emitted from the $1s$, $2s$, and $2p$ shells. He employed screened hydrogenic wave functions for the continuum electron and made his calculation for the case of β decay. Since similar calculations for the case of photo-ionization do not exist, we used his results for comparison with the experimental energy spectra.

IV. DISCUSSION OF RESULTS

Relative intensities of exciting more than one electron in the photoabsorption process as well as energy spectra of the electrons are deduced from Figs. 1–4. The total area under the profiles yields $P_1+P_s+P_s{}^*$, where P_1 is the number of single events represented by the photopeak, the x-ray satellite peak, and the tail of inelastic scattering losses, P_s is the number of double-ionization events given by the unshaded areas under the solid lines of the insets, and $P_s{}^*$ is the number of excitation-ionization events given by the shaded areas of the insets. We have normalized $P_1+P_s+P_s{}^*$ to unity. Strictly speaking, relative intensities obtained in this experiment refer to electron emission perpendicular to the x-ray beam and are independent of the emission angle only if the spatial distribution is the same for the observed quantities, viz., photoelectrons, *complementary* shakeoff electrons, and the less important inelastically scattered electrons. Since these angular dependences should be somewhat dissimilar relative to each other, we explored the degree of variation by the following experiment. We chose the most critical case in which the largest amount relative to the energy available is transferred to shakeoff processes, and measured the electron spectrum arising from Mg K_α x rays incident on neon under an angle of 45° between directions of electrons and photons. The fact that the resulting distribution agreed with that of Fig. 1 within the error limits allows us to consider P_1, P_s, and $P_s{}^*$ as fractional yields unaffected by the angle of observation. Values reported for these quantities are averaged from at least three runs for each experiment and associated errors account for uncertainties in statistics, analysis, profiles of inelastic losses, background level, and detection efficiency. No correction was applied for elastic or inelastic scattering into angles greater than the acceptance angle of the analyzer. At the electron energies dealt with here, such corrections made relative to the respective photolines can be neglected.[31]

TABLE I. Excitation and ionization of one or more electrons from L shell of neon accompanying K photo-ionization: probabilities per photon interaction (in percent).

	Excitation		Ionization	Total	
Shell	Expt.[a]	Theory[b]	Expt.	Expt.	Theory[c]
$2s$	⋯	⋯	⋯	⋯	1.9
$2p$	2±1	5	⋯	⋯	16.2
L	⋯	⋯	16.5±1.5	18.5±1.0	18.1

[a] Contains about 0.5 units for transitions $2p\rightarrow np$; $n\geq 4$.
[b] Transitions $2p\rightarrow 3p$ only, Eqs. (10) and (11); Refs. 30 and 32.
[c] Reference 32.

A. Double Electron Emission from Neon

In Table I the total intensity of removing an L electron from its orbit is compared with the intensity expected from the shakeoff theory.[32] The agreement is excellent. We see that in the majority of the events the shakeoff electron will go into the continuum as was suspected from earlier experiments[1–6,33] and theoretical

---

[30] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vol. II, p. 293. We owe the wave functions to C. Froese, University of British Columbia and the computational execution to C. W. Nestor of this laboratory.

[31] The change of the total scattering cross section is about 10% per 100 eV for the energy ranges reported [*Landolt-Börnstein Tables*, edited by A. M. Hellwege (Springer-Verlag, Berlin, 1950), Vol. I, pp. 327 and 343]; for changes of ionization cross sections alone see Ref. 21. Only a fraction of this change would bear on the data considering the operating pressure and the angular distribution of the scattered electrons [N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1965), 3rd ed., p. 564].

[32] According to Eqs. (5) and (8) with the use of Hartree-Fock wave functions for the appropriate initial and final states. For details see C. W. Nestor, T. C. Tucker, T. A. Carlson, L. D. Roberts, F. B. Malik, and C. Froese, Oak Ridge National Laboratory Report No. ORNL 4027, 1966 (unpublished); the use of P. S. Bagus's wave functions [Phys. Rev. **139**, A619 (1965)] yields identical results.

[33] T. A. Carlson, Phys. Rev. **130**, 2361 (1963).

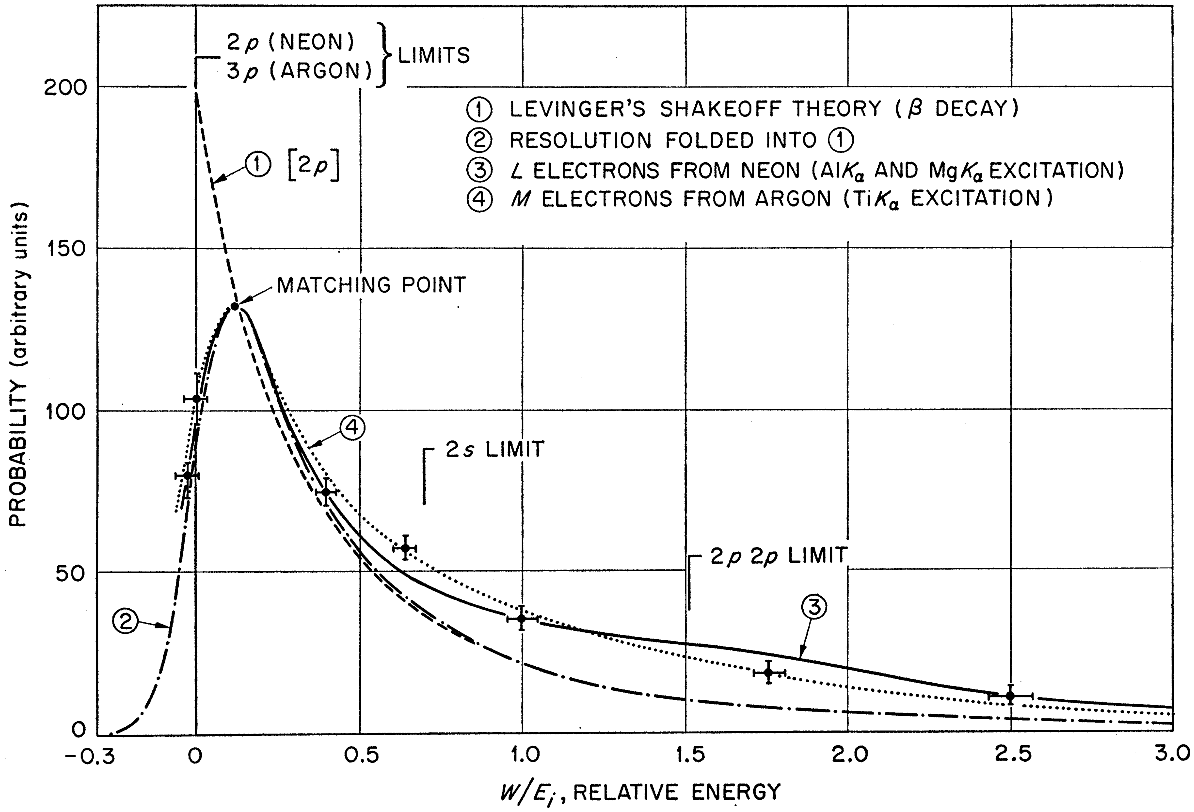

FIG. 5. Comparison of experimental energy spectra of shakeoff electrons from L shell of neon and M shell of argon with theoretical spectrum for $2p$ electrons. W=kinetic electron energy, E_i=ionization energy of emitted electrons. Error bars at selected points indicate possible spread of curves. Limits for $2s$ and $2p2p$ ionization of neon are estimated.

estimates.[34] For the relative probability of the transition $2p \rightarrow 3p$ we calculated 4.6% to the ^2S(lower) state of Eq. (10) and 5.7% to the ^2S(upper) state of Eq. (11). This excitation probability of about 5% is somewhat higher than the experimental intensity of (2±1)%. Also, a small excitation probability of 3.4% is calculated for the β decay $\text{Ne} \rightarrow \text{Na}^+$, and an experimental value of (2±0.5)% has been reported[35] for the decay $\text{Kr} \rightarrow \text{Rb}^+$. It appears to be a general feature that excitation by shakeoff in multielectron atoms is a rare event as compared to ionization.

TABLE II. Simultaneous excitation and ionization of one or more electrons from L and M shells of argon with photo-ionization of K electron: probabilities per photon interaction (in percent).

Shell	Expt.	Theory[a]
2s	···	0.3
2p	···	1.73
L	3.0±0.8 (2.5±0.8)[b]	2.03
3s	···	2.88
3p	···	17.65
M	20.7±1.4	20.53

[a] Reference 32.

[b] Value in parentheses is corrected for events of simultaneous shakeoff from L and M shell: $P_L \times P_M \approx 0.5$.

The ionization energy $E_{2p(K)} = (41 \pm 3)$ eV agrees reasonably well with the value of 45.2 eV calculated with Hartree-Fock (HF) wave functions[32,36] and with $E(\text{Na}\,\text{II}) = 47.3$ eV, which should be considered an upper limit. The excitation energy $E_{2p(K)}{}^*(2p \rightarrow 3p)$ is (32±2) eV.

B. Double Electron Emission from Argon

Analysis of Figs. 3 and 4 yields the intensity values listed in Table II. Again, satisfactory agreement is found between theory and experiment, provided a correction is made for simultaneous events of removing an L electron together with an M electron. The probability of these events is given approximately by $P_L \times P_M$, and they would appear in the spectrum of Fig. 4 at $\Delta E \gtrsim 350$ eV. As in the case of neon we find a small probability for excitation of outer electrons, namely about 3%, which is a small fraction of the total shakeoff probability of 20.7%.

The energies of $E_{2p(K)}$, $E_{3p(K)}$, and $E_{3p(K)}{}^*$ are summarized in Table III together with theoretical

---

[34] A. E. S. Green, Phys. Rev. **107**, 1646 (1957).

[35] H. J. Andrä, K. Luchner, and W. Schambeck, Z. Naturforsch **21a**, 1987 (1966).

[36] Obtained from the difference of the total energies of the configurations $\text{Ne}^+\ 1s2s^22p^6$ and $\text{Ne}^{2+}\ 1s2s^22p^5\ {}^3P$.

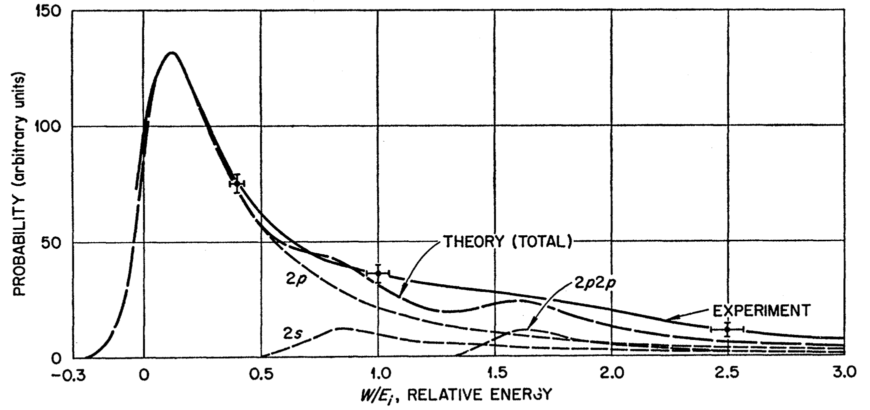

FIG. 6. Energy spectrum of L shakeoff electrons of neon compared to theoretical spectrum which is the sum of individual contributions from $2p$, $2s$, and $2p2p$ electrons. Spectra of $2p$ and $2s$ electrons are taken from Levinger (Ref. 7), that of $2p2p$ electrons is estimated.

values. Agreement between theory and experiment is good for the ionization energies, and the energy required to promote a $3p$ electron to the $4p$ level is the same as measured earlier[17] in a different type of experiment.

C. Energy Distribution of Electrons

Since the distributions $f(E_1)$ and $f(E_2)$ are mirror images of one another, we regard the threshold of $f(E_1)$ (ionization limits in Figs. 1–4) as the origin of a new positive energy scale of the kinetic energy W of the shakeoff electrons. To compare the spectra for neon and argon with each other and with theory we matched the curves at their maximum values, adjusted them to the same resolution, and plotted intensity versus the normalized energy W/E_i, where E_i is the ionization energy of the $2p$ electron of neon or the $3p$ electron of argon in a K-ionized atom. Figure 5 shows the result: The similarity of the experimental distributions is striking and correspondence to the theoretical prediction is satisfactory at energies up to about $W=E_i$. This is the energy range in which roughly 80% of the events occur. The enhancement of the experimental over the theoretical distribution at higher values of W/E_i can largely be accounted for by the onset of multiple shakeoff processes. In Fig. 6 we compare the distribution for neon with the theoretical spectrum that results from shakeoff of one $2p$, one $2s$, and two $2p$ electrons. Relative contributions were obtained[32] from Eqs. (5) and (7); the spectral shape for $2s$ and $2p$ electrons is taken from Levinger's calculation,[7] and that for the loss of two $2p$ electrons was assumed to be similar to the one for one $2p$ electron in terms of W/E_i. The over-all agreement between theory and experiment can be regarded as satisfactory, although undulations in the theoretical curve are not distinguishable in the experimental curve. Appraisal of the discrepancies should await experimental data of greater statistical certainty and improved theoretical calculations to be made for the case of photo-ionization with more accurate wave functions.

We note that the energy spectra of shakeoff electrons from the $2p$ shell of neon and the $3p$ shell of argon accompanying K ionization are similar to that of shakeoff electrons from the $2p$ shell of neon accompanying L ionization.[33] This and the over-all agreement with a theory[7] using hydrogenic wave functions suggests that characteristic parameters of the ejected electrons—or, from a theoretical point of view, the character of wave functions—exert no drastic influence upon the *energy distributions* normalized to W/E_i, although shakeoff *probabilities* depend decisively on the type of wave functions used. Earlier measurements by Suzor[16] and co-workers of electron shakeoff as a result of β decay seem to contradict the present findings, indicating a slower intensity drop with increasing energy. These authors were, however, unable to assess partial contributions from the various subshells and multiple events; they made no corrections for the (poor) energy resolution and perhaps insufficient corrections for scattered electrons and background, so that a direct comparison with theory or the results of this paper proves difficult.

D. Comparison with Data from Other Sources

A close relationship exists between the present data and the relative intensities of x-ray and Auger-electron satellites, intensities of different ion charges produced by inner-shell ionization, and the charge spectra resulting from β decay. We consider the various observed quantities as arising from the same cause, that is, a sudden perturbation of the atomic potential. The

TABLE III. Ionization energies in eV for $2p$ and $3p$ electrons and excitation energy for $3p$ — $4p$ in an argon atom with a hole in the $1s$ shell.

Transition	Expt.	Theory
$2p \rightarrow \infty$	300±10	305[b]
$3p \rightarrow \infty$	29±3	30.4[b]; 30.5[c]; 32[d]
$3p \rightarrow 4p$	22±3, 22[a]	···

[a] Reference 17; the value presumably refers to the energy difference of the systems $\mathrm{Ar}(1s2s^22p^63s^23p^64p)$ and $\mathrm{Ar}(1s2s^22p^63s^23p^54p^2)$.

[b] From total-energy differences of the atomic systems, calculated with relativistic Hartree-Slater wave functions.

[c] From total-energy differences with Hartree-Fock wave functions.

[d] Reference 11.

TABLE IV. Consequences of K ionization and KL ionization or excitation of neon as recorded by selected experimental methods.

	Observed quantities					
Initial event	Photoelectron(s) photon impact	Electron energy loss; electron impact	Photons	Auger electrons	Ion charges A^{a}	B^{b}
$K\to\infty$	Discrete line [see Eq. (1)]	Continuum with threshold[c] at $E=E_0-E_K$	K_α lines	K-LL lines	1+	2+
$K\to\infty$ $L\to\infty$	Two continua [see Eq. (3)]	Continuum with threshold at $E=E_0-E_K-E_{L(K)}$	K_α satellites	K-LL satellites (KL-LLL)	2+	3+
$K\to\infty$ $L\to M, N, \cdots$	Discrete lines [see Eq. (2)]	Continuum with threshold at $E=E_0-E_K-E_{L(K)}{}^*$	Satellites of K lines	K-LL and K-LX satellites	1+	2+

[a] By radiative readjustment. [b] By nonradiative readjustment. [c] E_0 = primary electron energy.

following can then be understood as a comparison of the various data with the results of the shakeoff theory.

We choose the example of neon to illustrate in Table IV which quantities can be observed by selected experimental methods when either K or KL vacancies have been created. According to the tabulation several methods can be employed to determine yields of K and KL ionization. The present method is particularly suited to probe also ionization and simultaneous excitation, and by its very nature, it is the only method for determination of energy distributions of the emitted electrons. Measurements of photons and Auger electrons (columns 4 and 5) are specific probes for initial ionization events regardless of the particular type of ionization process.

Numerical results from different experiments on neon are listed in Table V and compared with the predictions of the shakeoff theory and the present experimental results. In all experiments the change of the Hamiltonian has about the same magnitude and is sufficiently rapid[37] to justify the use of the shakeoff principle. Good agreement exists between theory and experiment except for the value of 23% for x-ray satellites which was obtained by the inherently less accurate method of photometry. We find, however, some smaller differences; e.g., promotion of L electrons occurs more often in β decay than in photo-ionization. This reflects the fact that the effective charge changes by one unit in β decay rather than by 0.85 units for K ionization. Measurements of ion charges in which excitation events are not observed give a slightly smaller value than this work in accord with the present finding that excitation processes are indeed rare.

TABLE V. Shakeoff probabilities (in percent) of L electrons of neon as measured by various methods. Comparison of data with results of shakeoff theory.

Method	Expt.	Theory
Photoelectrons (this work)	18.5±1	18.1[a]
Ion charges from photo-ionization[b]	17.4±1.2	16.1[a,b]
X-ray satellites electron impact	≈23[c]	17.5[d]
Auger satellites electron impact	14.5±2.5[e] 19.4±1.7[e]	18.1[a]
Orbital electron loss in β decay	20.1±1[f]	21.4[g]

[a] Reference 32.
[b] Reference 3; ionization events only. Theoretical value of 18.1% adjusted for excitation events which occur about 2% of the time.
[c] Extrapolated and renormalized from curve of L. G. Parratt, Phys. Rev. 50, 1 (1936).
[d] Reference 13.
[e] Reference 14; the second value stems from a recent experiment of Mehlhorn (private communication).
[f] Reference 33; value corrected for (calculated) probability of K electron emission; experiment registers ionization events only.
[g] Reference 32; contains excitation processes also. According to Sec. IV A, theory yields more than 3.4% for excitation events, a value which is probably too large considering the results on the related case of photo-ionization.

Table VI reports data for argon on photo-ionization, x-ray satellite production, and electron loss in β decay. Satisfactory agreement is again found between experiment and theory and among experimental data. Our study of double photo-ionization and Deslattes's[11] work on x-ray satellites allow us to associate K_α satellites with initial KL and K_β satellites with initial KM vacancies[38] and a subsequent single electron jump.

E. Intensities of K_α Satellites of Mg, Al, and Ti

As a byproduct of the present work, electron spectra of Figs. 1–3 yield relative intensities of K x-ray satellites of the elements Mg, Al, and Ti. It is curious to note that if we questioned the origin of x-ray satellites we would find these spectra to offer the rare opportunity of exhibiting at the same time both the effect, the satellite line, and its cause, double ionization (indicated by the continuous spectrum of complementary shakeoff electrons). Though the explanation is for a different element and a different excitation mode, the concept of electron shakeoff closes the apparent gap by describing double ionization as a general phenomenon.

---

[37] One may question this for ionization by electron impact, chiefly because most of the emitted K electrons have small energies relative to the ionization energy E_K. Even so, their energies are generally greater than those of L electrons, liable for shakeoff, considering the jump in ionization energies from one principal shell to the other (i.e., $E_K/E_{L(K)}\approx 20$ for neon).

[38] One type of K_β satellite that is due to KL vacancies would appear at much higher energies, near the K lines of the element $Z+1$, and has not been looked for.

Table VI. Electron loss from L or M shell of argon by sudden perturbation of atomic potential. Comparison of present data with data on x-ray satellites and β decay. Production probabilities (in percent) per interaction.

Shakeoff from shell	Photoelectrons this work		X-ray satellites		Orbital electron loss β decay	
	Expt.	Theory	Expt.	Theory	Expt.[a]	Theory[b]
L	2.5	2.0	2[c]	···	18±1	3.0
M	20.8	20.5	22±5[d]	20.8[e]		22.0

[a] T. A. Carlson, Phys. Rev. **131**, 676 (1963); only ionization events are registered.
[b] Reference 32; values comprise both ionization and excitation processes.
[c] L. G. Parratt, Phys. Rev. **50**, 1 (1936); electron impact.
[d] Reference 11; in fluorescence.
[e] Reference 13; change in oscillator strengths with hole configurations considered.

Table VII. Relative production probabilities (in percent) of K_α satellites of Mg, Al, and Ti.

Element	This work	Nordfors[a]	Parratt[b]	Theory
Mg[c]	13 ±1.5	···	13.5	9.7
Al[c]	8.5±1.5	7.4; 7.6	9.5	6.9
Ti	4 ±1.5	···	1.3	1.1

[a] Reference 39; first value for metal, second for oxide.
[b] L. G. Parratt, Phys. Rev. **50**, 1 (1936).
[c] *Note added in proof.* T. Åberg (private communication) draws my attention to additional determination for Mg and Al, and their oxides: V. F. Demekhin and V. P. Sachenko, in *Röntgenspectren und Chemische Bindung* (VEB Reprocolor, Leipzig, 1966), p. 58; D. W. Fischer and W. L. Baun, J. Appl. Phys. **36**, 534 (1965); and J. Utriainen, M. Linkoaho, E. Rantavuori, T. Åberg, and G. Graeffe (to be published). T. Åberg's refined theoretical values (to be published) agree well with these and the present experimental data.

In Table VII we compare the satellite intensities with literature data and theory. Measured intensities are probably characteristic of the metal oxides since Al and Mg targets were cleaned only every 20 to 24 h of operation and the Ti target was contained in a permanently sealed tube (Machlett AEG 50). Theoretical values are obtained from Eqs. (5) and (7) and refer to free atoms. Inclusion of solid-state and chemical effects and changes of oscillator strengths with hole configurations[13] would alter the quoted values, though to a small degree. Nevertheless, theory accounts satisfactorily for satellite intensities reported here and by Nordfors.[39]

V. CONCLUSIONS

Energy spectra of electrons that are emitted from neon and argon atoms in the photoabsorption process have been measured and the following results and conclusions have been obtained: (a) The ejection of more than one electron by a single photon has been observed directly; (b) this process occurs in about 20% of the events for the combinations KL(Ne) and KM(Ar), and in about 2% for KL(Ar); (c) excitation of an outer electron in a monopole transition and simultaneous ionization of an inner electron occurs infrequently, namely in about 2% of the events; (d) one electron is emitted with an energy close to that of the photoelectron of the single photo-ionization process, whereas the other electron(s) is (are) emitted with small energies; (e) the energy distribution of the continuum electrons that originate from the less tightly bound shells, the shakeoff electrons, is such that the majority possesses kinetic energies of less than their ionization energies; and (f) the present data are well accounted for by the electron-shakeoff theory.

Comparing the present results and related data from other sources with data on double-electron emission from the outermost shells[19,20] of rare-gas atoms, we find that the shakeoff theory yields good results if the two electrons come from different shells, but it fails if the electrons both come from the outer shell or perhaps from the same inner shell.[40] Present data together with those of Deslattes[11] implicate multiple ionization in *specific* shells with a subsequent single electron jump as the origin of *specific* x-ray satellites and, by way of analogy, of Auger-electron satellites. As a byproduct of the measurements, relative intensities of K_α x-ray satellites of Mg, Al, and Ti were obtained. Also these data agree satisfactorily with the results of the shakeoff theory.

ACKNOWLEDGMENTS

We wish to thank B. Nestor and T. Tucker of this laboratory for calculating wave functions, overlap integrals, and energies of atomic states used in this paper. We are also indebted to C. Froese of the University of British Columbia for making available to us wave functions for excited Ne$^+$ and Na$^+$ configurations.

---

[39] B. Nordfors, Arkiv Fysik **10**, 279 (1956).

[40] H. Primakoff and F. T. Porter, Phys. Rev. **89**, 920 (1953); T. A. Carlson, C. W. Nestor, T. C. Tucker, and F. B. Malik, Phys. Rev. (to be published).