where a_0 = radius of the first Bohr orbit, ρ = electron density, Z_ie = nuclear charge on the ith atom, and r_i = distance from the nucleus of the ith atom. The values of the constants are $\kappa_k=(3/10)(3\pi^2)^{2/3}e^2a_0$ and $\kappa_a=(3/4)(3/\pi)^{1/3}e^2$. In order, the terms are the kinetic energy of the electrons, the electron interaction energy, the electron and nuclei interaction, and the electron correlation energy. By use of maximizing and minimizing conditions, Abrahamson *et al.* have obtained a form amenable to calculation with an error not exceeding 4% relative to the TFD approximation. The interatomic potential is in terms of H

$$V(r)=Z_1Z_2e^2/r+H-H(\infty), \qquad (12)$$

where Z_1 and Z_2 are the nuclear charges and $H(\infty)$ is the electronic energy at infinite separation. Again from Ref. 6, the reduced form of the potential is

$$\begin{aligned}V(r)=(Z_1Z_2e^2/2r)[\Psi(Z_1^{1/3}r/a)+\Psi(Z_2^{1/3}r/a)]\\ +\tfrac{1}{6}\iiint\{\kappa_k[(\rho_{01}+\rho_{02})^{5/3}-(\rho_{01}^{5/3}+\rho_{02}^{5/3})]\\ -2\kappa_a[(\rho_{01}+\rho_{02})^{4/3}-(\rho_{01}^{4/3}+\rho_{02}^{4/3})]\}dv, \qquad (13)\end{aligned}$$

where Ψ = TFD screening function, ρ_{0i} = exact undistorted electron density for the ith atom, and $a=0.8853a_0$. The integration is performed over the region of overlap of the electron clouds.

The TFD interaction potential $V(r)$ was calculated according to Eq. (13) for the system $\mathrm{Li^+}$-He on an IBM 7074 digital computer. The values of the ionic and atomic radii and the corresponding electron densities ρ_{0i} were obtained from a set of tables computed by Thomas.[18] A six-point Lagrangian interpolation procedure was used to obtain the radii, and a four point interpolation the electron densities for integral values of Z from the Thomas tables. The determinations of $V(r)$ was done for internuclear separations of $0.1a_0$ to $1.7a_0$, the latter determined by the TFD radii. These results are shown in Table I and also as the dashed curve in Fig. 5.

On comparing the TFD calculated $V(r)$ with the experimental, the agreement is seen to be fairly good, with the TFD value about 4 eV higher than the experimental for the range of separations down to about 0.35 Å. Below this the calculated $V(r)$ becomes increasingly too large. The work done by Abrahamson for various noble gas atom systems also shows such a disparity between the TFD values and experimental results for very small internuclear separations. The results of the TFD calculation by Abrahamson for He-He are also included in Table I for comparison with those for $\mathrm{Li^+}$-He.

ACKNOWLEDGMENTS

The assistances of L. Gray in the computer programming and of W. C. Giffen in the construction and testing of the apparatus is gratefully acknowledged.

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[18] L. H. Thomas, J. Chem. Phys. **22**, 1 (1954).

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Electron-Impact Ionization Measurements of Surface-Ionizable Atoms*

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Total electron-impact ionization cross-section measurements are presented for calcium, strontium, barium, and thallium. These and previously determined cross sections for the alkali metals are compared with available techniques for calculating cross sections. Because of the difficulty of both the experimental measurements and the calculations, it is perhaps surprising to find agreement generally better than a factor of 2.

I. INTRODUCTION

THEORETICAL work by Rudge and Seaton[1] has aptly demonstrated the limited accuracy and difficulty of wave-mechanical calculations for predicting the ionization of atomic hydrogen by electron impact. Calculating other atomic-ionization probabilities by these methods is obviously more complex. In contrast, the semiclassical methods discussed by Gryziński[2] are simple and, while not completely understood, useful. Gryziński has shown the agreement between semiclassical calculations and experiment for the ionization of H, H_2, and He. In all instances the agreement was perhaps better than one might expect. Other theoretical work of classical or empirical origin includes that of Thomson,[3] Elwert,[4] Drawin,[5] and Lotz.[6] Stafford[7]

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] M. R. H. Rudge and M. J. Seaton, Proc. Roy. Soc. (London) **A283**, 262 (1965).

[2] M. Gryziński, Phys. Rev. **138**, A305 (1965).

[3] J. J. Thomson, Proc. Cambridge Phil. Soc. **23**, 839 (1909).

[4] G. Elwert, Z. Naturforsch **7a**, 432 (1952).

[5] H. W. Drawin, Z. Physik **164**, 513 (1961).

[6] W. Lotz, Institut für Plasma-physik, Garching Bei München Report, 1966 (unpublished).

[7] F. E. Stafford, J. Chem. Phys. **45**, 859 (1966).

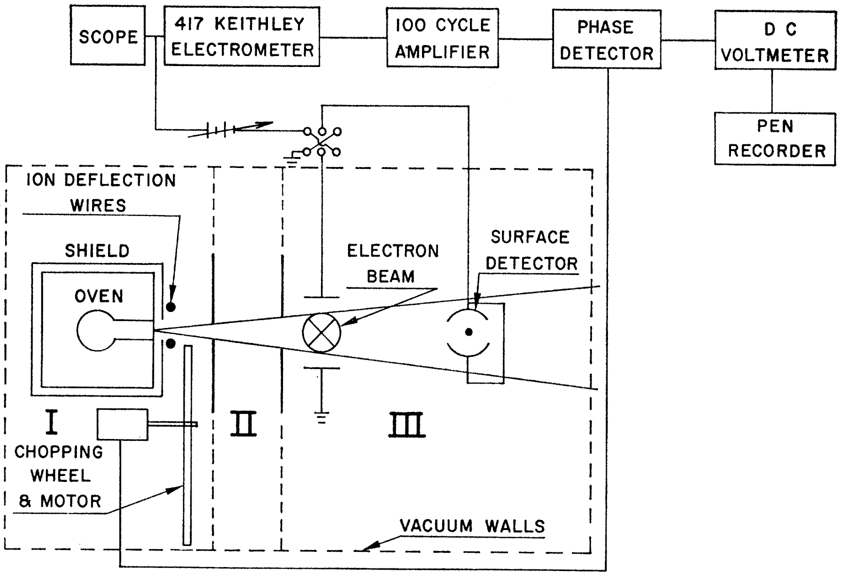

FIG. 1. A block diagram of the experimental system including the necessary electronics.

has compared the known ionization cross sections at 60 eV with Gryziński's computations.

In work by McFarland and Kinney,[8,9] the total ionization cross sections of the alkali metals were measured by electron impact. Surface ionization of the metals on tungsten or tungsten oxide was used for determining the atom beam flux. By normalization, one can deduce from the work of Tate and Smith[10] and Brink[11] the magnitudes of the cross sections for the singly and multiply charged ions.

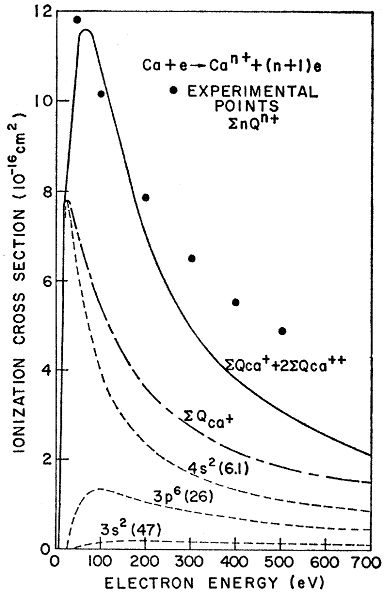

FIG. 2. Total ionization cross section for calcium versus electron energy. The Gryziński partials and sums are shown for comparison.

Subsequent work[12] involved a remeasurement of the absolute cross section of lithium and sodium, in which the atom-flux and surface-ionization efficiencies were measured directly by weighing the metal used and monitoring the atom beam intensity until it was depleted. The new cross sections were within the experimental error previously reported, thus giving credence to earlier assumptions concerning surface ionization reflection coefficients.

On the basis of this work measurements were made on the total electron-impact ionization of calcium, strontium, barium, and thallium. Choice of these materials was based on the ability of the apparatus to simultaneously produce an atomic beam and measure its density.

The purpose of this paper is to present that experimental work, and to compare it and earlier work with some of the available theory.

II. APPARATUS AND PROCEDURE

The apparatus and procedure followed in this experiment has been discussed previously.[8] For completeness, it involved a chopped crossed-beam experiment in which the electron beam was buried in the atomic beam. The density of the atomic beam was determined in terms of the surface ionization of the beam on hot tungsten. As previously, the Saha-Langmuir equation was used for calculating the surface-ionization efficiency. The tungsten temperature was determined by use of Jones-Langmuir tables. In effect, all reflection coefficients in the Langmuir-Saha equation were assumed zero, although this is a more stringent assumption than necessary.

A schematic of the experiment is shown in Fig. 1.

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[8] R. H. McFarland and J. D. Kinney, Phys. Rev. **137,** A1058 (1965).

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[10] J. T. Tate and P. T. Smith, Phys. Rev. **46,** 773 (1934).

[11] G. O. Brink, Phys. Rev. **127,** 1204 (1962).

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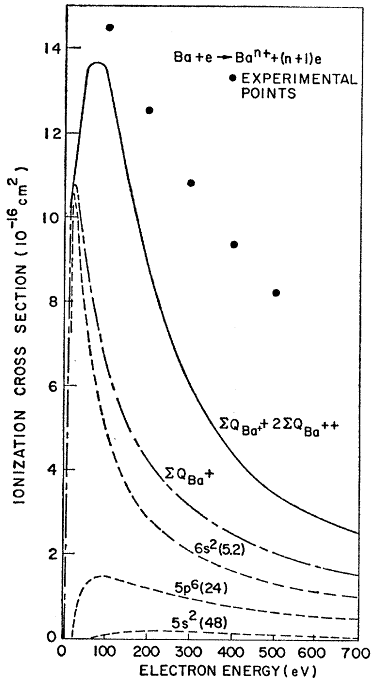

Fig. 3. Total ionization cross section for barium versus electron energy.

III. RESULTS AND DISCUSSION

Total ionization electron-impact cross sections for calcium, strontium, barium, and thallium are to be observed as experimental points at 50, 100, 200, 300, 400, and 500 V in Figs. 2, 3, 4, and 5. While experimental work does not exist from which one can normalize to provide a separation of the various degrees of ionization, one can use Gryziński calculations to gain further information of the processes. This has been done in Figs. 2, 3, and 4 in which the calculated contributions of the individual shells and their sum for the ions of unit charge are shown. Also shown in these figures is the total unit-charge ionization cross section added to twice the cross section for double ionization. The calculated double-charge ionization cross section calculations are shown in Fig. 6. Figure 7 presents our present knowledge of cesium, while Fig. 8 shows a comparison between experiment and theory for double ionization in the alkali metals. Figure 5 includes the Gryziński partials and their sum for the single and twice the double ionization processes for thallium. The details of the Gryziński calculations are as follows:

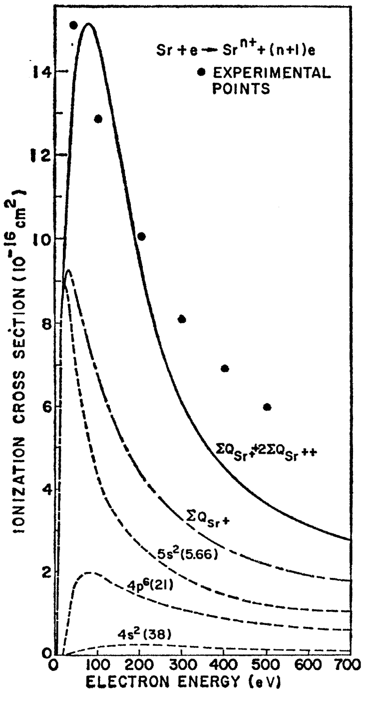

Fig. 4. Total ionization cross section for strontium versus electron energy.

In its simplest form the energy-dependent electron-impact cross section for the removal of a single electron

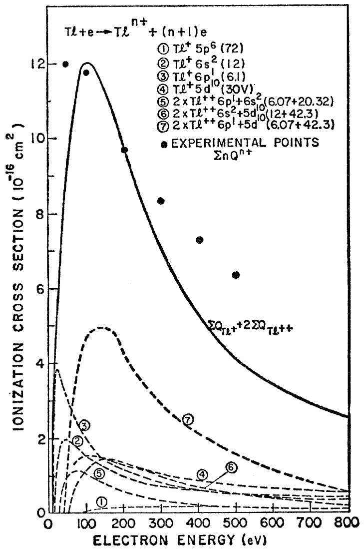

Fig. 5. Total ionization cross section for thallium versus electron energy.

from an atom can be represented by

$$Q_{\mathrm{atom}^+}(E)=\sum_k N_k Q^k(E,U_k),$$

$$Q^k(E,U_k)=(6.56\times10^{-14}/U_k^2)\,g(E/U_k),$$

$$g(x)=x^{-1}[(x-1)/(x+1)]^{3/2}\times\{1+\tfrac{2}{3}[1-(2x)^{-1}]\ln[2.7+(x-1)^{1/2}]\}. \quad (1)$$

In this representation, U_k is the binding energy in eV of the ionization process being considered. E is the energy of the impacting electron, and N_k is the number of electrons requiring a given minimum energy for the removal from the atom. One must sum over the closed shells of the atom as well as the valence electrons although, in practice, only the valence electron and the outermost closed shell contribute appreciably to the cross section.

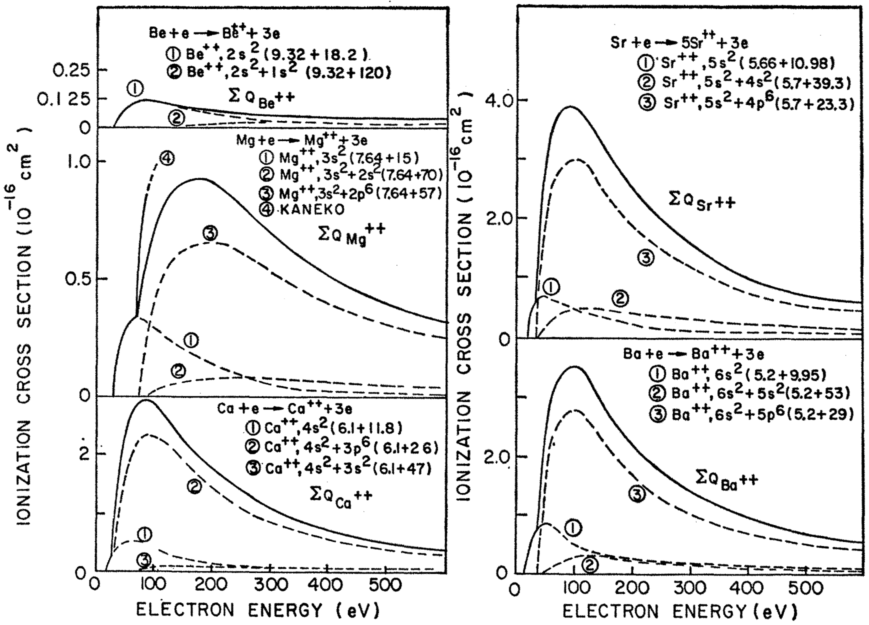

FIG. 6. The double-ionization cross sections versus electron energy for the alkaline earths.

The cross section for double ionization is

$$Q_{\text{atom}^{++}}(E)=\sum_k Q^k(U_1, U_2),$$

$$Q^k=\frac{(6.56\times10^{-14})^2}{U_1^2U_2^2}\,\frac{N_e(N_e-1)}{\pi r^2}\,g\left(\frac{E}{U_1+U_2}\right), \tag{2}$$

where U_1 is the binding energy of the first ejected electron and U_2 is binding energy of the second ejected electron in the field left by the removal of the first. N_e is the number of electrons in a specific energy state for which a transfer from the incidence electron of a quantity of energy, (U_1+U_2), would give rise to double ionization. The quantity r is the mean radius of the atomic system having N_e electrons.

In this work, since simplicity was desired, it has been assumed that to a first approximation the effective atomic radius[13] could be determined in terms of the energy U_i necessary to remove the valence electron,

$$r=14.3\times10^{-8}/U_i. \tag{3}$$

A second assumption involved the assignment of a binding energy to an inner-shell electron, providing that the atom is ionized. First and second ionization energies are available from the tables compiled by Moore.[14] Binding energies of inner electrons (neutral atoms) are generally available from tables compiled by Bearden.[15] Second ionization energies involving these inner electrons were assumed to be greater than the binding energy by an amount equal to the difference between the first and second ionization energy. The involved electron configurations and the assumed effective energies (U_1+U_2) are indicated with the partial-ionization curves.

The total-ionization experimental points of Figs. 2, 3, 4, and 5 show reasonable agreement with the sums of the partial-ionization curves for the first and second ionization species. The agreement is poorest in the high-energy range where contribution of higher multiplicity of ionization is neglected. However, only with

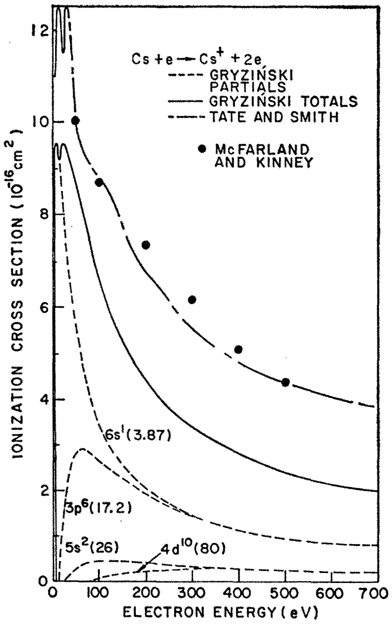

FIG. 7. The electron-impact ionization cross section versus electron energy for cesium. By comparison, Witting reports a maximal value of about 15 Å² and a 50-eV value of about 12.2 Å² Heil and Scott measure a 50-eV value of 5.3 Å².

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[13] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York and London, 1934), p. 102.

[14] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. Government Publishing and Printing Office, Washington 25, D.C., 1949).

[15] J. A. Bearden, Oak Ridge National Laboratory Report No. NYO-10586, 1964 (unpublished).

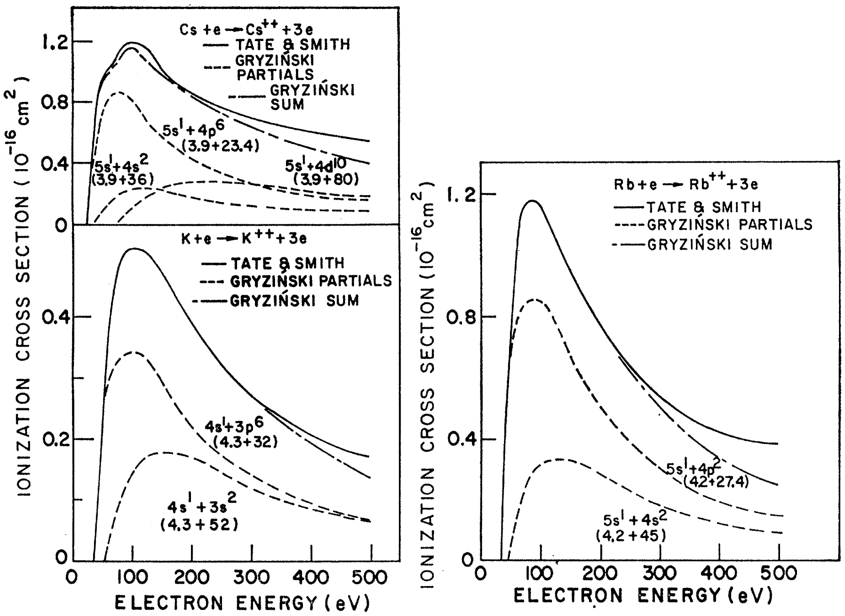

FIG. 8. The double-ionization cross sections of cesium, potassium, and rubidium versus electron energy. Tate and Smith relative curves have been normalized to the quantitative measurements of McFarland and Kinney.

barium does the disagreement become as great as a factor of 2.

The calculated double ionization of magnesium is compared in Fig. 6 with previously measured results of Kaneko.[16] Kaneko's relative measurement was normalized in Fig. 6 to the calculated curve determined by using Eq. (3) for obtaining r. A better fit results from allowing the effective radius for $3s^2+2p^6$ electrons to be smaller than for the $3s^2$ electrons. A best fit to Kaneko's data would require

$$r_{p+s}\sim r_s/\sqrt{2}\sim 2.5a_0. \tag{4}$$

The threshold step to be seen in the double ionization of calcium and strontium has been qualitatively observed by Fiquet-Fayard and Zeisel[17] and Kaneko and Kamomata.[18] While no experimental double-ionization evidence is known for beryllium, its calculated cross section is shown in Fig. 9 for completeness, as are the summed cross sections for beryllium and magnesium. The larger value of r_{p+s} has been used for magnesium. The double-ionization cross sections of potassium, rubidium and cesium as measured by Tate and Smith and normalized to values of McFarland and Kinney are compared in Fig. 8 with calculated values. Since these cross sections were known, it was possible to adjust r to obtain a somewhat better fit than in previous examples.

Kieffer and Dunn[19] have compiled experimental data and discussed in detail some of the problems involved in ionization measurements. In these crossed-beam experiments utilizing surface ionization as a means of determining neutral beam density, errors arise from three principal sources. These are the possibility that the reflection coefficients in the Langmuir-Saha equation are not in effect zero, that the geometry factors of the beam are not accurately determined, and that measurements of ionization currents are somehow incorrectly made. The reflection coefficients r_i of the incident cold atom on the surface, and r_a and r_+ of the hot atom and ion from the surface, have been measured by the author for lithium and sodium, by Schroen[20] for potassium, and by Langmuir and Kingdon[21] for cesium. Indications are that for each of these metals,

$$(1-r_i)=(1-r_a)/(1-r_+)=1,$$

or in effect,

$$r_i=r_a=r_+=0. \tag{5}$$

Obviously, to assume zero reflection for the other metals is subject to future investigations and the possibility of normalizing their cross sections in the light of new information.

The geometry factors were computed by standard techniques.[22] The works of Brink[11] and of McFarland and Kinney[8] were performed on two different systems with different vacuum conditions, different chopping speeds, and different electronic circuitry for measurement. In addition, the distances between slits, electron

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[16] Y. Kaneko, J. Phys. Soc. Japan **16**, 2288 (1961).

[17] F. Fiquet-Fayard and J. P. Ziesel, in *Proceedings of the Sixth International Conference of Ionization Phenomena in Gases* (S.E.R.M.A., Paris, 1964), Vol. 1, p. 37.

[18] Y. Kaneko and I. Kamomata, J. Phys. Soc. Japan **18**, 1822 (1963).

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[21] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. (London) **107**, 161 (1925).

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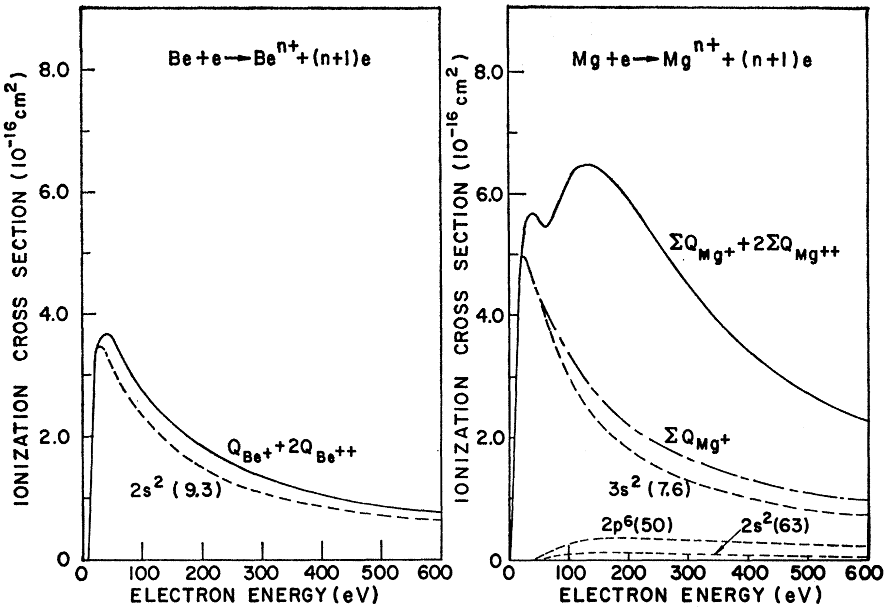

FIG. 9. The electron-impact ionization cross sections for beryllium and magnesium versus electron energy, as computed with Gryziński's equations.

beam, and surface detectors were intentionally changed and geometries recalculated. In all cases the resultant total cross sections were within the experimental error of about 10%.

Experimentally, the ionization currents are the most difficult entities to measure. The electron-induced ion current I_i was of the order of 10^{-11} A. The surface detector current I_{sd} was 10^4 times larger. Fortunately, I_i appeared only in the calculations as a ratio of I_i/I_{sd}. Each of these could be measured by use of a 100-cycle ac amplifier and phase detector. A calibrated resistor string was used for reducing I_{sd} to a signal strength comparable with I_i. The absolute value of I_{sd}, easily measured either with a dc electrometer or an oscilloscope, was necessary for the calculation of the neutral-atom velocity, but the velocity was a slowly changing function of I_{sd}.

The apparent agreement between Gryziński computations and the work in this laboratory (all performed and reported before we were aware of semiclassical calculations) doesn't necessarily prove the quantitative correctness of either. It is interesting that qualitatively there is exceedingly good agreement to the point of predicting major structure.

There is only a limited amount of research, either theoretical or experimental, with which this work can be compared. Lithium has been treated theoretically by McDowell and co-workers[23–25] and Peach,[26] using Born and modified Born approximations. Drawin,[5] Gryziński,[2] Burgess,[27,28] and Lotz[6] have used semiclassical and empirical relationships in work on lithium. A somewhat simplified compilation of their results can be seen in Fig. 10. Burgess in a personal communication indicated that his calculation was normalized to the McDowell *et al.*[25] results at a sufficiently high energy that a Born-approximation calculation should be valid. Thus Burgess's result which compares qualitatively with the experimental measurements should have a validity limited only by the sophistication of the calculation of McDowell *et al.*[25]

Burgess[28] has verbally suggested that the ratio of approximately two between his calculations and the experimental cross section for lithium may also exist for all of the alkali metals.

The only other known cross-section measurements which may be compared are those of Witting,[29] and Heil and Scott[30] (Brink's have been compared previously). Witting's measurement on cesium involved the use of an ionization gauge technique and comparison at 150 eV with the cross section of N_2. Heil and Scott[30] extrapolated this result to 50 eV, and reported a cross section of 12.2 Å^2. The reported value from the author's laboratory of 10.1 Å^2 is within the sum of the experimental errors of the two experiments.

On the other hand, the 5.3 Å^2 value reported by Heil and Scott from their 0–26 eV measurements extrap-

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[23] M. R. C. McDowell and G. Peach, Phys. Rev. **121**, 1383 (1961).

[24] G. Peach and M. R. C. McDowell, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 277.

[25] M. R. C. McDowell, V. P. Meyerscough, and G. Peach, Proc. Phys. Soc. (London) **85**, 703 (1965).

[26] G. Peach, Proc. Phys. Soc. (London) **85**, 709 (1965).

[27] A. Burgess, in Proceedings of the Symposium Atomic Collision Processes in Plasmas, Culham Laboratory, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-R4818, 1964, p. 63 (unpublished).

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[29] H. L. Witting, in Proceedings of Thermionic Conversion Specialists Conference, NASA, Lewis Research Center, Cleveland, Ohio, 1964 (unpublished).

[30] H. Heil and B. Scott, Phys. Rev. **145**, 279 (1966).

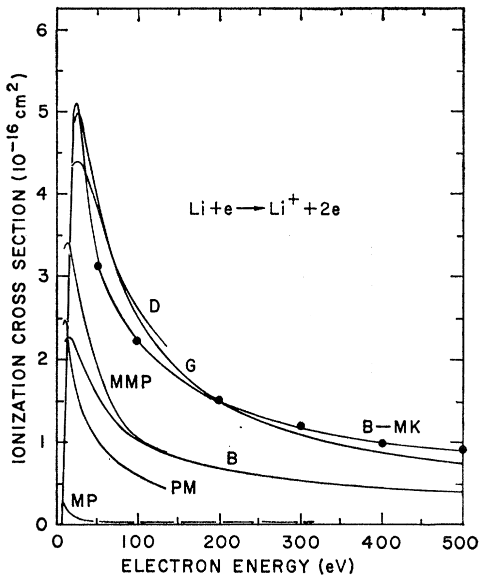

FIG. 10. A summary of post-1960 measurements and calculation of the electron-impact ionization cross sections of lithium. MP: McDowell and Peach (Ref. 23); PM: Peach and McDowell (Ref. 24); MMP: McDowell, Myerscough, and Peach (Ref. 25) and Peach (Ref. 26). All of these are Born or modified-Born calculations. B refers to the work of Burgess (Ref. 27). G is a Gryziński (Ref. 9) calculation using equation developed and discussed (Ref. 2) subsequent to 1960. This distinction is made, as earlier work did not exhibit the proper high-energy dependence. D refers to Drawin's (Ref. 5) empirical calculation. B-MK is Brink's (Ref. 11) relative curve normalized to McFarland and Kinney's (Ref. 8) experimental points at 500 eV.

olated to 50 eV is not. This contradiction has not been explained to date. The assumptions used for determining the cesium neutral-atom densities are the same in both experiments; however, the methods are different. Current measurements are rendered difficult in the Heil and Scott experiment because of insulator problems. This difficulty is not experienced in a crossed-beam experiment. Heil and Scott have discussed this problem in detail with respect to the ion current generated by the electron beam and have taken precautions to prevent an erroneous measurement. They have not discussed the measurement of positive ions from the surface ionizer or how the potentials for collection of ions and heating the tungsten wire are prevented from influencing their results. This is particularly important as number densities of the order of 7×10^{10} cm^{-3} (2.6×10^{-6} Torr) are higher than would be expected at room temperature (1.1×10^{-6} Torr) and certainly less than expected at 350°K (1.2×10^{-4} Torr).

Marino *et al.*[31] have studied the surface-ionization detector in a cesium atmosphere in detail and have succeeded in keeping glass insulators showing 10^{12} Ω resistance under somewhat comparable circumstances. This suggests the current leakage described by Heil and Scott as due to absorbed cesium may be due to adsorbed cesium which should contribute to a higher vapor pressure.[31] Marino has remarked in a personal communication that he was unable to obtain meaningful density results by immersing the detector in the vapor and was required to utilize beam techniques for this measurement.

Because of the evidence of condensed cesium present in both the interaction- and surface-detection regions and the lowness of the measured number density in relationship to the enclosure temperature, one may question whether the two regions separated by the electron collector can be assumed to have comparable fluxes. Heil and Scott have associated a steady state with cessation of a transport of cesium and have said, "spatial gradients of density, temperature and pressure can be present, but the flux j_n is constant throughout." With j_n (number cm^{-2} sec^{-1}) $=\frac{1}{4}n\bar{v}=\frac{1}{4}n$ $(1.262\times 10^3\ T^{1/2})$, it is not clear how j_n can be constant and n vary spatially at 350°K.

Even were the cesium density measurement in error, this would not explain the differences in experimental results, as a greater density leads to a smaller Heil-Scott cross section. On the other hand, if such an error exists, its cause could be of the same origin as that which could cause an error in either the electron or ion current measurement. Unguarded collectors could provide such a source of error.

In summary, surface-ionizable atoms from periods 2 and 3 of the periodic table have been ionized by electron impact and, through beam-density normalization measurements using surface ionization, ionization cross sections have been determined. While limited experimental measurements in periods 2 and 3 are available for comparison, it is possible to compare the results of previous measurements on period 1 elements with measurements of Brink and of more recent work on cesium. In all cases comparisons have been generally better than a factor of 2. The same can now be said of all recent theoretical work. The best agreement is with Gryziński's calculations.

Note added in proof: K. Omidvar and E. C. Sullivan, Goddard Space Flight Center, have recently completed calculation of ionization cross sections of selected many-electron atoms by electron collision. These results have been submitted for presentation at Leningrad at the Fifth International Conference on the Physics of Electronic and Atomic Collisions.

Of lithium, Omidvar has written the author, "Asymptotically our calculation agrees with your measurement. At low energies the calculated cross section is higher than measurement. This is expected since Born approximation is used in our calculation."

It is interesting that this Born calculation disagrees by approximately a factor of 3 with the Born calculation of McDowell, Meyerscough, and Peach[25] at the highest energy common to both.

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[31] L. L. Marino, A. C. H. Smith, and E. Caplinger, Phys. Rev. **128**, 2243 (1962).