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MEASUREMENT OF CROSS SECTIONS FOR IONIZATION BY ELECTRON IMPACT AT LOW VAPOR PRESSURES

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A technique is developed for studying ionization by electron impact in substances having low vapor pressures. The apparent ionization cross sections for lead, copper, and silver are measured at energies from the ionization threshold up to 150 eV. The results agree satisfactorily with theoretical calculations. The fine structure observed in the initial segment of the ionization function of lead may be due to autoionization.

INTRODUCTION

ALTHOUGH ionization by electron impact has been investigated for more than forty years, only about fifteen elements have been studied with sufficient thoroughness; these are mainly gases and metals that exhibit high vapor pressures at relatively low temperatures. Most of the elements in the periodic table have not been studied at all in this connection, because no sufficiently simple and reliable technique has been available for investigating the ionization by electron impact of elements whose physical properties do not resemble those of gases.

The principal complications of the appropriate investigations arise because it is difficult to obtain a sufficiently stable and high atomic concentration of the investigated element in the ionization chamber and to perform reliable measurements. Atomic beams comprise the most efficient means of introducing neutral atoms having low vapor pressure into the ionization region. This method of determining ionization cross sections was first used by Funk,[1] whose method of calculating concentrations led to considerable errors in his values of the absolute ionization cross sections.

The atomic beam method was subsequently used by numerous investigators to study the ionization of gases, and particularly to measure the cross sections for the ionization of atoms in molecular gases.[2-5] Despite the improvement of the technique (the use of modulated atomic beams to separate the useful signal from the ion currents of residual gases), the concentrations of neutral atoms were not determined in any of the aforementioned studies. In each case absolute cross sections were obtained by means of calibration based on the data of other investigators. The simultaneous measurement of the absolute neutral-atom concentration and of the ion production was first performed in[6]; the atomic concentration was measured by means of tagged atoms. For a similar purpose Brink[7,8] has used a surface-ionization detector that is suitable for a limited number of elements, mainly alkali metals.

At the present time we have absolute measurements of ionization cross sections for all the alkali metals except francium. It was of decided interest to study the ionization of metals in the copper subgroup; we would thus be enabled to compare the behavior exhibited by the ionization functions of two subgroups belonging to a single group, and also the absolute cross sections.

EXPERIMENTAL TECHNIQUE

Our method of measuring the cross sections for atomic ionization by electron impact is as follows. The investigated atomic beam and a beam of monoenergetic electrons cross in the ionization region. The total amount of ions produced in this way is determined from the ion current, and the neutral-atom concentration is determined from the atomic beam intensity. In order to separate the ionic current of the test element from that of residual gases the atomic beam is modulated and the variable component of the ion current is measured.

The apparatus used to study the ionization of metallic ions is a vacuum chamber enclosing the neutral atom source, the electron source, the ion collector, and the neutral-atom collector (Fig. 1). The atomic beam source 1 is an effusive-

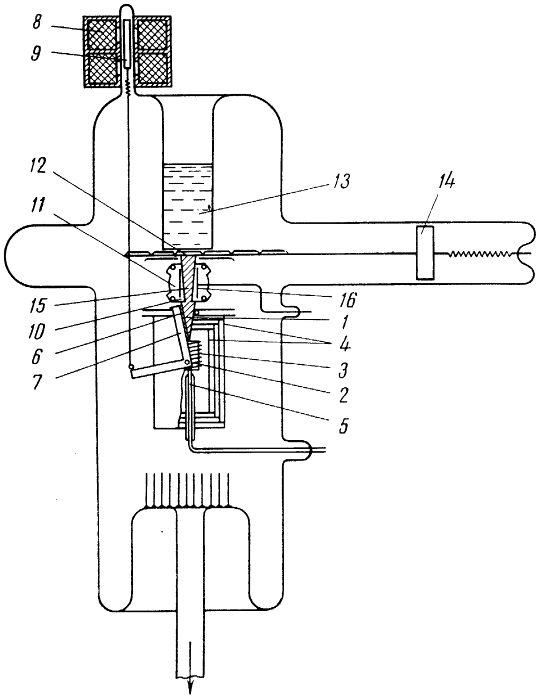

FIG. 1. Apparatus for determining the ionization cross sections of metallic ions having low vapor pressure.

flow vessel 2 heated by a bifilar tungsten heating coil 3. The vessel is surrounded by four cylindrical radiation shields 4, and its temperature is measured by a platinum—platinum-rhodium thermocouple 5 that is welded to the vessel.

The atomic beam is first bounded by holes in the tops of the radiation shields. Two electrodes 6 remove charged particles from the atomic beam; such particles can be formed during the evaporation of the test element. The atomic beam is chopped by the chopper 7, which is actuated by an external electromagnet 8 with an iron core 9 that is connected to the chopper. The atomic beam now passes through the collimating diaphragm 10 into the ionization region 11 of the electron source, before striking and condensing on the neutral-atom collector 12 that has six plates pressed tightly (for the purpose of being cooled) against the flat bottom of a Dewar 13 in the upper portion of the instrumental envelope. The collector is connected to the iron ring armature 14 used to exchange the plates in the course of the experimental work. Within the ionization chamber the atomic beam 1 crosses the electron beam 15; the resulting ions are extracted by the ion collector 16.

In the present work we used effusive-flow vessels having a 0.6-cm long aperture located 3.5 cm from the electron beam; the atom concentrations obtained in the ionization region were of the order 10^{11}—10^{12} atoms/cm^3. Our experimental work was based on molecular evaporation from the source; therefore the form of the beam and the intensity distribution over its cross section depended only on the sizes and mutual separation of the source aperture and the collimating diaphragms.[9]

The mass of the condensate was determined by weighing the collector plates to within 10^{-5} g. The deposition rate and neutral-atom concentration in the ionization region were quite stable, with maximum deviations of 4—5% from their mean values. The procedure of determining the concentration by weighing the condensed material is based on the assumption that all the neutral atoms are deposited on the collector. At collecting plate temperatures below 575°C the condensation coefficient is unity for copper and silver.[10,11] The condensation coefficient of lead deposited on a nickel plate was measured in a broad temperature range.[12]

We tested several types of electron sources and obtained the best results with a "tetrode" source and beam focusing by a 300—500 gauss uniform longitudinal magnetic field. With this design of the electron source, the beam encounters no electrodes in its entire path from the cathode to the collector. Thus the possibility of secondary electron emission is completely eliminated and errors in measuring the electron current are obviated. In addition, the electron energy spread in the beam is determined completely by the initial energy spread of electrons emerging from the cathode. Our measurements1) indicate that the latter spread is 0.25—0.5 eV depending on the operating conditions; our electron source was operated with an initial energy spread not exceeding 0.25 eV. In calculating the ionization cross sections we took into account the complete electron path, whose length differed from the distance traveled by electrons along the magnetic field by not more than 1.6% at the minimum beam energy (7.5 eV).

In the present work the modulated ion current was measured with an electrometer amplifier (U-1-2) and ÉNO-1 oscilloscope. Prior to the measurements, the amplifier sensitivity was calibrated and its frequency characteristic was determined;2) the sensitivity of the cathode-ray oscilloscope was also calibrated.

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1)The electron energy spread was observed with two types of electron velocity selectors, a Hughes-Rojansky electrostatic selector and a uniform magnetic field selector.

2)The 0.5—1 cps modulating frequency of the atomic beam was selected on the basis of the frequency characteristic of the U-1-2 amplifier.

In the course of our experimental work we checked the completeness of ion extraction and frequently recorded the dependence of the ion and electron currents on the electron-accelerating voltage. The collector plate was changed every 30—40 minutes; measurements were performed in the same sequence until all the plates had been used.

In the present work all quantities required for cross section measurements were determined experimentally. The cross section was computed from the formula

$$Q_{i\ \mathrm{app}} = \frac{I_i}{I_e}\frac{tm\bar{v}b}{M_c}, \qquad (1)$$

where I_i is the ion current, I_e is the electron current, M_c is the mass of condensate, m is the test-atom mass, t is the deposition time, $\bar{v}$ is the mean velocity of beam atoms, and b is the width of the atomic beam in the region traversed by the electron beam.

The ion current measurement error is composed of the 2.6% error in calibrating the sensitivity of the electrometer amplifier and the 5% error in measurements of the amplifier output signals. The relative error of the time measurements is under 0.5%. The error in determining the mean atomic velocity $\bar{v}$ in the beam is at most 0.25%. The relative geometric error does not exceed 1%. The error of electron current measurements is 1.5%, and that of the condensate mass measurements is under 1%. The results showed that the condensation rate was constant to within 4%. The total (maximum) error of the ionization cross section measurements is thus 15%, while the rms error is under 10%. The spread of our experimental curves did not exceed the foregoing computed error.

EXPERIMENTAL RESULTS AND DISCUSSION

We employed our technique to measure the ionization cross sections of lead, copper, and silver using ionizing electron energies from 7 to 150 eV. In Fig. 2 curve 4 shows the dependence of the ionization cross section of lead on the electron energy E. Points on the curve were obtained by averaging twelve experimental curves; the vertical bars denote the average spread of the curves. For Pb the maximum ionization cross section is 8×10^{-16} cm^2 at E = 55 eV, and its rate of increase near threshold is 0.7 $\times 10^{-16}$ cm^2/V; 50% of the maximum is reached at 6 eV above the threshold. We can thus infer that the 0.35-eV electron energy spread introduces no important error in the measurement of the ionization function.

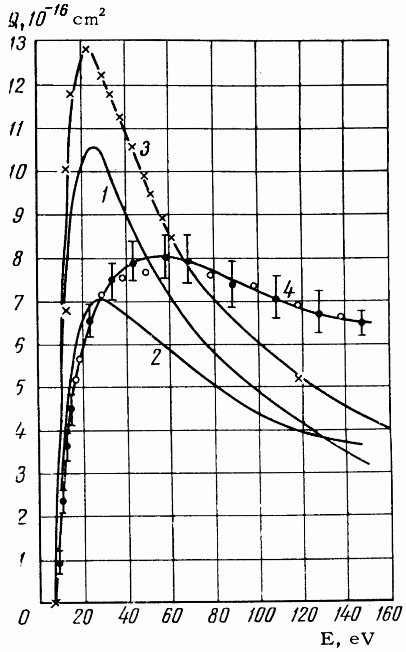

FIG. 2. Measured ionization cross sections of lead (curve 4) and theoretical curves based on equations of Gryzinski [27] (curve 1) and Drawin, [28] in addition to a calculation based on the Born approximation (curve 3).

The behavior of the ionization cross section near threshold is of marked interest. In the case of mercury, Lawrence[13] observed a number of maxima in the initial segment of the curve, and a maximum was found at 10.8 eV in[14,15]. Similar irregularities have been observed in the cases of zinc, cadmium,[15] magnesium,[16] argon,[17] copper, silver, and gold.[18]

The behavior of the initial segment of the ionization curve is of theoretical interest. Wannier has established[19] that the single-ionization cross section Q is proportional to the power 1.127 of the excess energy. Geltman[20] developed a theory predicting the linear change of the ionization cross section near its threshold. Most earlier measurements[3,16,21] and those in our present work also confirm Geltman's law (Figs. 2, 4, and 5). A detailed analysis of the ionization function of lead has indicated the existence of a fine structure near the threshold (Fig. 3), manifested by a deviation from linearity. This structure can be attributed to autoionization. Indeed, the lead atom possesses energy levels[22] located above the ionization threshold (Fig. 3) in the region of the ionization function that exhibits the fine structure.

Figure 4 shows the ionization curve of copper. The initial segment is linear, and the rate of

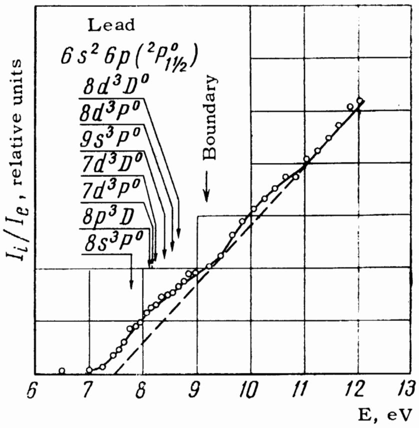

FIG. 3. Initial segment of the ionization function of lead.

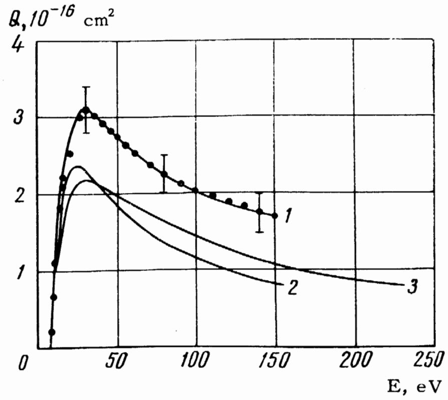

FIG. 4. Our measurements of the ionization function of copper (curve 1) and theoretical curves based on equations of Gryzinski (curve 2) and Drawin (curve 3).

change of the cross section near threshold is 0.45×10^{-16} cm²/V.

The ionization curve of silver from 7 to 150 eV is shown in Fig. 5. The initial segment here resembles that for copper and exhibits a similar rate of change (0.47×10^{-16} cm²/V), although the curve descends more slowly following the maximum than in the case of copper. Our earlier measurements of the ionization cross section of silver[6] agree within error limits with the present work, where, however, we have not studied the fine structure of the ionization functions of copper and silver near threshold. Blais and Mann,[18] who measured the relative ionization cross sections of copper, silver, and gold from threshold to 12 eV, observed only inappreciable deviations from linearity in the threshold regions of the respective ionization functions.

As a check on our technique we measured the ionization cross section of mercury using the modulated atomic beam technique and the level-occupation technique. The absolute ionization cross sections measured by these two methods

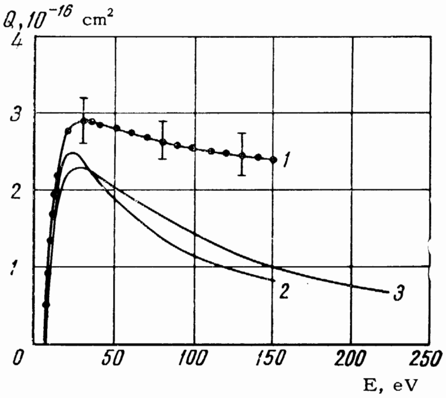

FIG. 5. Our measurements of the ionization function of silver (curve 1) and theoretical curves based on equations of Gryzinski (curve 2) and Drawin (curve 3).

coincide within the error limits and also agree with the results obtained by other investigators.[14,23-26] We thus have evidence that no systematic error sources exist in our present technique.

Our experimental results were compared with different theoretical calculations based on the classical approximation of Gryzinski[27] and the semiempirical formula of Drawin[28] (Figs. 2, 4, and 5). For lead we also calculated the ionization cross section in the Born approximation using the model proposed by L. A. Vaĭnshteĭn.[3] The calculation based on Drawin's equation yielded the best agreement with experiment. The Gryzinski formula and the Born approximation produce a steeper rise at the beginning of the curve, and their maxima exceed the experimental function by 30–60%. With 150-eV electrons the calculated cross section comprises 60–70% of the measured value. One cause of this discrepancy may be the formation of multiply-charged ions in view of the fact that the calculated functions express the dependence of the cross sections of singly-charged ions on the energy of the ionizing electrons, while the measured function represents the behavior of the apparent ionization cross section at different electron energies. If we assume that at 150 eV, which equals ~20 E_i (E_i is the ionization threshold) the cross section for single ionization corresponds to the Born-approximation calculation (4.2×10^{-16} cm²), then the multiply-charged ion current comprises 35% of the total ion current, in agreement with Bleakney's data.[25]

When calculating the ionization cross sections of copper and silver using the formulas of Gryzinski and Drawin, we took into account only

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[3] The authors are deeply indebted to L. A. Vaĭnshteĭn for providing a program to be used for the given calculation.

the ionization from the outer shell (4s for Cu and 5s for Ag). This probably accounts for the fact that, unlike the case of lead, the calculated curves here lie below the experimental curves, since the closeness of the 4s and 3d levels of copper and the 5s and 4d levels of silver permits ionization involving the electrons of the 3d and 4d levels, respectively. The maximum ionization cross section computed from the Gryzinski formula is 25% smaller than the measured value for copper and 15% smaller for silver. A calculation based on the Drawin formula with the constants f_1 and f_2 equal to unity yields maximum cross sections of both metals that are about 30% smaller than the experimental values. This Drawin formula considers only the detachment of a single outer electron, whereas in our case double ionization is also possible. From the comparison of experiment and calculations we can infer that most of the apparent ionization cross sections of copper and silver represents the removal of only one electron from the outermost shell.

The experimental information that is available at the present time does not permit unique conclusions regarding the relationship between the electron configuration and the shape of the ionization function for the atom of any element. For this purpose we evidently require the absolute ionization cross sections for not only a single group, but for at least one entire period of the table of elements; unfortunately we do not now possess this knowledge.

In conclusion we wish to express our gratitude to M. A. Mazing and V. A. Fabrikant for discussions, and to B. N. Klyarfel'd for several valuable comments. We must also mention that the present problem was proposed by V. L. Granovskiĭ and the basic results were obtained under his guidance.

CONCLUSIONS

1. The apparent ionization cross sections of lead, copper, and silver were measured using electron beams having energies from the ionization threshold to 150 eV. The maximum ionization cross sections and the corresponding electron energies are: for lead, 8×10^{-16} cm^2 and E = 55 eV; for copper, 3.1×10^{-16} cm^2 and 29 eV; for silver, 2.9×10^{-16} cm^2 and 29 eV.

2. Satisfactory agreement was obtained when the ionization cross sections were compared with calculated values based on the formula of Gryzinski, the semiempirical formula of Drawin, and a Born approximation.

3. The ionization functions of lead, copper, and silver are linear near the ionization threshold. The initial segment of the ionization function of lead exhibits a fine structure than can be accounted for by autoionization.

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