

Electron-impact-ionization cross sections of the Ga and In atoms

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Absolute electron-impact cross sections for single, double, and triple ionization of gallium and indium have been measured from 0 to 200 eV. Beams of Ga and In atoms are formed by charge-transfer neutralization of 3-keV-ion beams with triethylamine or xenon. The cross sections are considerably larger than previous measurements and are also larger than the predictions of various empirical formulas and classical and quantum-mechanical theories, due in part to significant contributions from autoionization. The double-ionization cross sections appear to be dominated by ionization of a *d* electron followed by autoionization, rather than by direct double ionization.

I. INTRODUCTION

Although electron-impact-ionization cross sections for neutral atoms at the far left and right of the Periodic Table (groups I, II, VII, and VIII) are now reasonably well known,¹⁻³ there are only a few measured ionization cross sections for neutral atoms in the middle columns.¹ Thus, theory cannot be tested in this part of the Periodic Table, and cross sections predicted for many atoms by classical, empirical, and approximate quantum-mechanical calculations are of unknown reliability.

Available measurements of double and triple ionization of neutral atoms are even more scarce than measurements of single ionization, and the theory less well developed. The trend observed in the rare-gas² and halogen atoms³ is that the ratios of multiple-ionization to single-ionization cross sections increase for heavier atoms. Thus, we expect reasonably large multiple-ionization cross sections for Ga and In.

In this paper we report measurements of single, double, and triple electron-impact-ionization cross sections for the Ga and In atoms. The only previous measurements of Ga and In cross sections⁴⁻⁶ differ significantly from the present results.

II. EXPERIMENT

The apparatus has been described in detail previously.^{2,7} However, two improvements have been made for measuring the neutral-beam flux. One is an improved method for measuring background. Previously, the background was determined by closing a solenoid-controlled valve between the source and the detector chambers, which generated a large transient in the lock-in amplifier due to electrical noise. The improved method is to measure the background by detuning the Wien filter to a setting at which there are no observable mass peaks. This background is typically less than 5% of the signal from the mass-selected species. Additionally, any background from neutrals which form prior to mass selection by the Wien filter is subtracted out. These neutrals would introduce an error in a measured cross section because they

would contribute to the neutral-flux measurement but not to the ion measurement.

The second improvement is to correct for a small offset in the output of the lock-in amplifier (1–4 μV referred to the input) which measures the output (neutral flux) of the pyroelectric detector. Although this effect is insignificant for “intense” neutral beams (over about 50 μV), it does affect the cross section calculated from weaker beams. (In all of our previous work, the neutral beams were intense enough that the offset was negligible.) The correction procedure is to plot 10 to 15 measured cross sections versus lock-in output and determine the offset (an additive constant) so that the measured cross section is independent of neutral-beam flux. Measurements at higher neutral-beam flux are weighted more heavily since they have a better signal-to-noise ratio. This procedure has greatly improved the reproducibility and accuracy of cross sections measured with weak beams.

The Ga-ion beam was prepared in one of two ways, with the solid source feature of the Colutron ion source⁸ using crushed crystalline GaP in a neon discharge (or argon discharge in some of the earlier measurements), or with Ga metal in a CCl_4 discharge. Ions were extracted through a pinhole in the anode, accelerated to 3 keV, and Ga^+ was mass selected with the Wien velocity filter. The resulting Ga^+ beam had a measured current of 100 nA 30 cm beyond the end of the Wien filter.

Neutral Ga was prepared by charge-transfer neutralization of Ga^+ with triethylamine (TEA), which has an adiabatic ionization potential of 7.2 eV and a vertical I.P. of 8.1 eV (Ref. 9) (Fig. 1). (Our early measurements also used xenon and cyclopropane which have I.P.'s of 12.1 and 10 eV, respectively.) None of these gases has an I.P. resonant with the I.P. of Ga at 6.00 eV. Although charge transfer with TEA may neutralize ground-state Ga^+ with an energy defect of at least 1.2 eV, it seems more likely that charge transfer neutralizes the metastable $3d^{10}4s4p^3P^o$ state of Ga^+ which lies 5.91 eV above the ionic ground state and therefore 11.91 eV above the ground state of neutral Ga. This process should be near resonant with the ground state of Xe and resonant with excited states of cyclopropane and TEA. The photoelectron spectrum of TEA, for example, shows a broadband

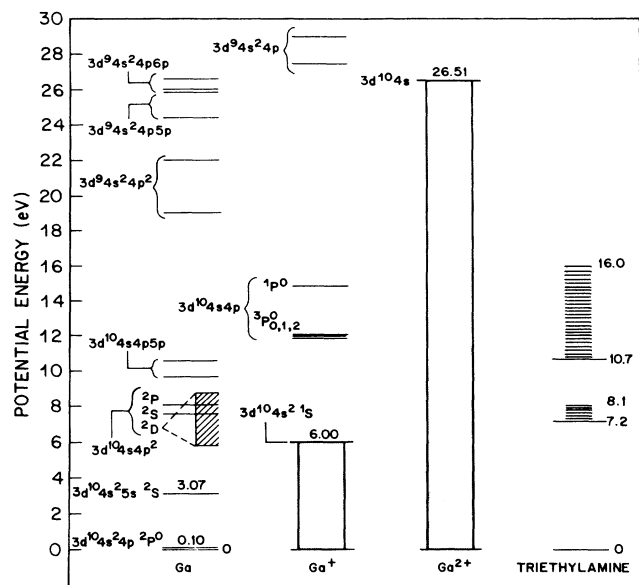


FIG. 1. Potential-energy diagram showing the electronic states and near-resonant charge-transfer neutralization of Ga⁺ by triethylamine.

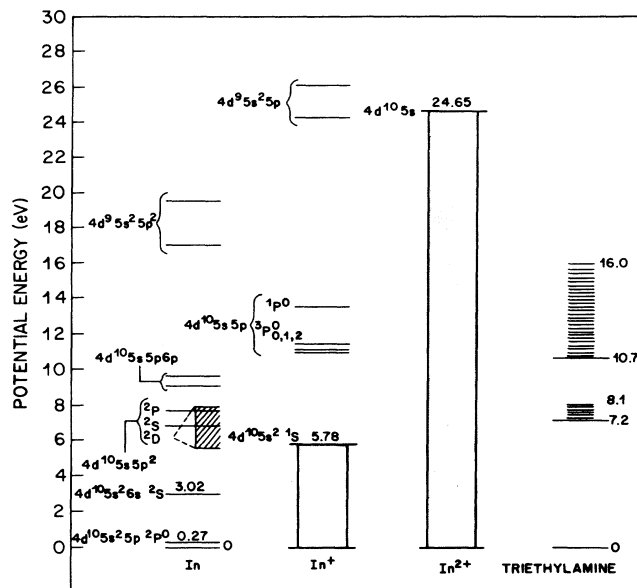


FIG. 2. Potential-energy diagram showing the electronic states and near-resonant charge-transfer neutralization of In⁺ by triethylamine.

ranging from 10.7 to 16 eV.¹⁰ Although both fine-structure components of the ground state should be populated, the fine-structure splitting is only 0.10 eV and cannot be resolved in our experiment. The mass spectrum of the neutral Ga beam (obtained by sweeping the voltage in the Wien filter to select ions before neutralization and detecting only neutrals after charge transfer) shows the expected 60:40 ratio for masses 69 and 71, confirming the identity of the beam as Ga.

Preparation of the In ion and neutral beams was similar to that for Ga, with crushed InP placed in a neon discharge or metallic In in a CCl₄ discharge. The metastable 4d¹⁰5s⁵5p³P^o state (or possibly the ground state) was neutralized by charge transfer with TEA to produce a neutral beam of In in the ²P ground state (Fig. 2).

A small background from ionization of Rydberg states, formed by charge-transfer neutralization of Ga⁺ and In⁺, was observed below the ground-state ionization thresholds. Appropriate corrections have been made.²

III. RESULTS

Absolute cross sections were measured for single, double, and triple ionization of Ga and In (although the triple-ionization data are only approximate since the signals were very weak). The procedure was first to measure the single-ionization threshold, to verify that the neutral beam was in its ground electronic state. Relative cross sections were then measured from 0 to 200 eV, followed by absolute cross sections for single ionization. Finally, the ratios of double-to-single and triple-to-single ionization were measured at several electron energies. The absolute measurements and ratios were used to normalize the relative 0–200-eV measurements.

A. Thresholds

Cross sections in the threshold region for single ionization of Ga and In are shown in Fig. 3. The threshold energies agree well with the known ionization potentials, 6.00 and 5.78 eV, respectively. The energy scales were calibrated with Eq. (1) of Ref. 11, which accounts for space-charge and contact potentials. Curvature at threshold is no more than about 0.5 eV, consistent with the energy spread of the electron beam and the small

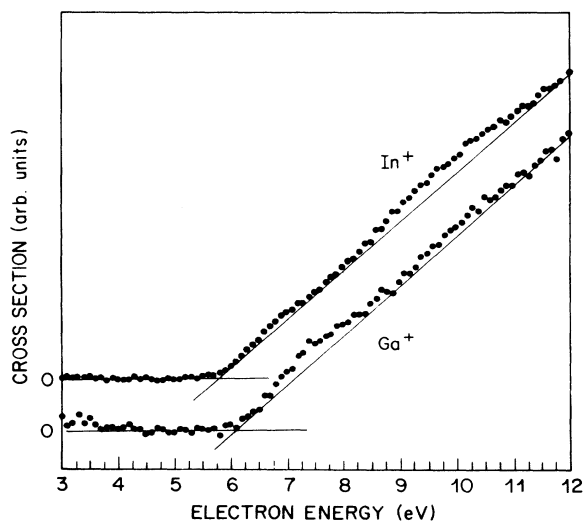


FIG. 3. Thresholds for single ionization of Ga and In.

ground-state fine structure of 0.1 and 0.27 eV for Ga and In, respectively.

Excited states are absent from the neutral beam, as demonstrated by Fig. 3 which shows no signal below threshold other than a negligible contribution from ionization of Rydberg states. Since the lowest excited states (2S) lie about 3 eV above the ground state, their presence would be easily detected by their ionization thresholds at only about 3 eV. Moreover, their lifetimes should be much shorter than the $\sim 5 \mu\text{s}$ time of flight to the electron beam, so they are not expected to survive.

The threshold region for double ionization of In is shown in Fig. 4(a). The energy scale has been corrected for the effects of space charge and contact potential. The In^{2+} threshold is at about 26 eV, slightly above the 24.65-eV spectroscopic double-ionization energy.¹² Similarly, the Ga^{2+} threshold is found at 28 eV, just above the 26.51-eV spectroscopic double-ionization energy.¹³

Triple ionization (Figs. 5 and 6) is too weak for meaningful thresholds to be measured. It appears that the major thresholds are in the range of 70 to 80 eV, significantly above the spectroscopic triple-ionization energies^{12,13} of 57.21 eV for Ga^{3+} and 52.68 eV for In^{3+} .

B. Cross sections

Relative cross section for formation of the single, double, and triple ions were measured at electron energies from threshold to 200 eV at 1-eV intervals. Two independent runs were corrected for measured variations in the electron current and then added together to improve the signal-to-noise ratio. Above 30 eV, measurements at several adjacent energies are averaged. Shape corrections, less than 5%, were also made below 50 eV and above 150 eV according to Eq. (15) in Ref. 2.

Absolute cross sections for single ionization are given in Tables I and II. The one-standard-deviation statistical uncertainty for 9 Ga measurements at 70 eV is $\pm 4\%$ and for 11 In measurements is $\pm 6\%$. Combined in quadrature with our previously determined systematic uncertainty of $\pm 12\%$,⁴ this yields overall uncertainties of $\pm 13\%$.

Ratios of cross sections at several electron energies for multiply charged to singly charged ions are also given in

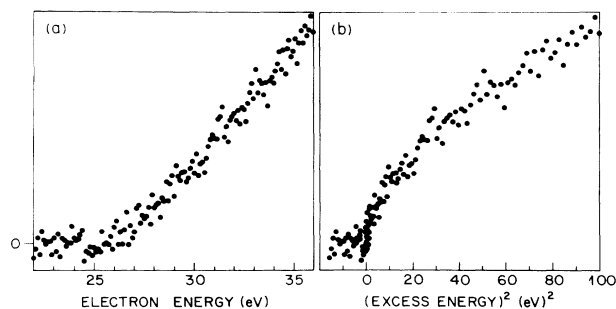


FIG. 4. Threshold for double ionization of In: (a) plotted on a linear energy scale, and (b) plotted against the square of the energy in excess of 26 eV.

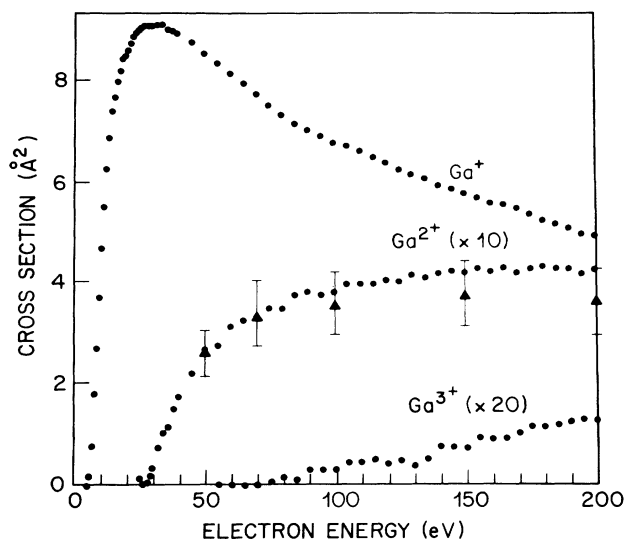


FIG. 5. Electron-impact-ionization cross sections for Ga.

Tables I and II. The uncertainties, which are dominated by measurement statistics, are $\pm 6\text{--}9\%$ (one standard deviation) for the double- to single-ion ratios and $\pm 12\%$ for the triple- to single-ion ratios.

The 0–200-eV shapes for formation of the single ions were normalized to the absolute cross section at 70 eV, and the shapes for double and triple ionization were normalized to the single-ion cross section at the appropriate energy using the measured ratios. The results are presented in Table III and Figs. 5 and 6.

Measurements at other electron energies of multiple- to single-ionization ratios are also given in Tables I and II and are indicated by solid triangles and error bars in Figs. 5 and 6. These serve to confirm the 0–200-eV shapes.

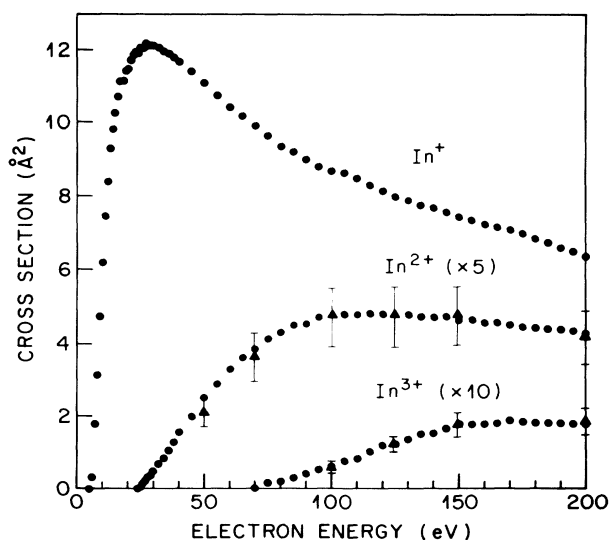


FIG. 6. Electron-impact-ionization cross sections for In.

TABLE I. Measured Ga cross sections and ratios.

Electron energy (eV)	Cross section for single ionization (\AA^2)	Ratios of cross sections $\sigma(\text{Ga}^{2+})/\sigma(\text{Ga}^+)$ $\pm 9\%$
50		0.030
No. of values		3
70	8.26 ± 0.34	0.043
No. of values	9	3
100		0.052
No. of values		3
150		0.065
No. of values		3
200		0.073
No. of values		2

IV. DISCUSSION

A. Indirect ionization

Excitation autoionization is known to contribute prominently to the ionization cross sections of ions, frequently dominating the cross section for higher stages of ionization.¹⁴ The present data show that such two-step processes also contribute to the cross sections for ionization of neutral Ga and In.

Near threshold, excitation-ionization structure appears in both the Ga and In cross sections (Fig. 3). Ga shows a weak feature about 1 eV wide around 7.5 eV and a possible one around 10 eV; In shows a feature around 6.8 eV and a broader one between 9 and 11 eV. Our data agree with previous observations of these features.^{15,16} The 7.5-eV Ga feature is probably due (Fig. 1) to autoionization of the $4s4p^2\ ^2S$ state at 7.70 eV, the $4s4p^2\ ^2P$ state at 8.2 eV,¹⁵ and the $4s4p^2\ ^2D$ resonance between the ionization potential and 8.8 eV.^{17,18} A possible Ga feature around 10 eV could represent autoionization of states of

the $3d^{10}4s4p5p$ and $3d^{10}4s4p6p$ configurations.¹⁹ For indium, the 6.8-eV feature is probably due (Fig. 2) to autoionization of the $5s5p^2\ ^2S$ state at 7.33 eV, the $5s5p^2\ ^2P$ state at 7.46 eV, and the $5s5p^2\ ^2D$ resonance between the ionization potential and 7.8 eV.^{12,20} The 9–11-eV indium feature lies in the region of several additional resonances, $5s5p(^3P^o)6p^2S$ at 9.67 eV, $5d5p(^3P^o)7p^2S$ at 10.5 eV, and $5s5p(^3P^o)8p^2S$ at 10.9 eV.^{12,19,21}

Small but reproducible peaks about 10 eV wide appear in the single-ionization cross sections (Figs. 5 and 6) centered at about 111 eV for Ga and 105 eV for In. There is also a noticeable change in the slope of the single-ionization cross sections above about 90 eV for both Ga and In which may be due to the onset of excitation-ionization processes or to ionization of the Ga 4p or In 5p electron.

Double ionization of both Ga and In appears to occur by a two-step ionization-autoionization process as recognized by Vainshtein *et al.*⁶ Ionization of a Ga 3d electron leads to a series of states in the 27–29-eV region with the configuration $3d^94s^24p$, above the 26.51-eV threshold for double ionization.²² Similarly, ionization of a 4d electron of In leads to states in the 24–26-eV region with the configuration $4d^95s^25p$ most of which are above its double-ionization potential of 24.65 eV.²³ The functional form of the cross section at threshold should carry information about whether double ionization is dominated by direct double ionization or an indirect ionization-autoionization process. Direct double ionization is expected to give a threshold which increases as the square of the excess energy, whereas single ionization of a d electron followed by autoionization should give a linear threshold. A plot of the double-ionization signal against the square of the excess energy in Fig. 4(b) shows much stronger curvature than Fig. 4(a), suggesting that direct double ionization of In is weaker than single ionization of a 4d electron followed by autoionization. A similar contribution of d-electron ionization to double ionization has been discussed for the isoelectronic ions Sn^+ and Sb^{2+} .^{24,25}

Triple ionization could also have major contributions from indirect processes. The process would be single ionization followed by two sequential Auger decays. For Ga or In, respectively, single ionization is expected to involve ionization of a 3p electron with an orbital ionization potential in the 109–122-eV range or ionization of a 4p electron with an orbital I.P. in the 81–95-eV range (Table IV), followed by the sequential emission of two electrons.

TABLE II. Measured In cross section and ratios.

Electron energy (eV)	Cross section for single ionization (\AA^2)	Ratios of cross sections	
		$\sigma(\text{In}^{2+})/\sigma(\text{In}^+)$ $\pm 6\%$	$\sigma(\text{In}^{3+})/\sigma(\text{In}^+)$ $\pm 12\%$
50		0.038	
No. of values		2	
70	9.91 ± 0.56	0.078	
No. of values	11	5	
100		0.11	0.007
No. of values		2	2
125		0.12	0.016
No. of values		1	2
150		0.13	0.024
No. of values		2	2
200		0.13	0.030
No. of values		2	2

B. Comparison to previous measurements

There are two previous reports of Ga and In cross-section measurements,^{4–6} both of which disagree with each other and with the present results. The total cross-section measurements by Zapesochnyi *et al.*^{4,5} differ significantly in shape from our present measurements (Fig. 7), where our total ionization cross sections are given as $\sigma^+ + 2\sigma^{2+} + 3\sigma^{3+}$. For each atom, we observe a single peak and monotonic falloff, as for most other atoms, rather than a low-energy peak or shoulder and

TABLE III. Cross sections (\AA^2) for electron-impact single, double, and triple ionization of Ga and In.

Energy (eV)	Ion					
	Ga ⁺	Ga ²⁺	Ga ³⁺	In ⁺	In ²⁺	In ³⁺
6	0.17			0.31		
7	0.72			1.78		
8	1.73			3.17		
9	2.61			4.74		
10	3.59			6.19		
11	4.55			7.45		
12	5.36			8.39		
13	6.10			9.29		
14	6.74			9.81		
15	7.25			10.26		
16	7.54			10.72		
17	7.85			11.13		
18	8.06			11.14		
19	8.30			11.43		
20	8.36			11.48		
21	8.48			11.72		
22	8.66			11.87		
23	8.76			11.95		
24	8.89			11.91		
25	8.91			12.07	0.01	
26	8.93			12.05	0.03	
27	8.94			12.17	0.04	
28	8.98	0.01		12.13	0.06	
29	9.00	0.02		12.14	0.07	
30	9.04	0.03		12.12	0.09	
32	9.14	0.07		12.07	0.13	
34	9.19	0.10		11.98	0.17	
36	9.13	0.12		11.91	0.21	
38	9.15	0.15		11.79	0.25	
40	9.14	0.18		11.68	0.31	
45	9.06	0.23		11.42	0.40	
50	8.92	0.28		11.10	0.51	
55	8.74	0.29		10.76	0.58	
60	8.62	0.33		10.44	0.67	
65	8.45	0.34		10.19	0.73	
70	8.26	0.35		9.91	0.77	0.01
75	8.08	0.37		9.64	0.83	0.02
80	7.90	0.37	0.01	9.36	0.86	0.02
85	7.77	0.40	0.00	9.21	0.90	0.03
90	7.68	0.40	0.02	9.00	0.91	0.04
95	7.56	0.40	0.01	8.80	0.94	0.05
100	7.44	0.40	0.02	8.69	0.94	0.06
105	7.42	0.42	0.02	8.63	0.96	0.08
110	7.32	0.42	0.02	8.48	0.96	0.08
115	7.21	0.42	0.03	8.30	0.96	0.10
120	7.09	0.43	0.02	8.13	0.96	0.12
125	6.97	0.42	0.03	7.99	0.96	0.12
130	6.89	0.44	0.02	7.87	0.96	0.14
135	6.80	0.42	0.03	7.75	0.95	0.15
140	6.74	0.44	0.04	7.68	0.94	0.15
145	6.67	0.45	0.04	7.56	0.95	0.17
150	6.57	0.44	0.04	7.45	0.93	0.18
155	6.54	0.45	0.05	7.35	0.93	0.18
160	6.41	0.45	0.05	7.24	0.92	0.18
165	6.39	0.45	0.05	7.16	0.92	0.18
170	6.33	0.44	0.05	7.10	0.90	0.19
175	6.19	0.45	0.06	7.00	0.89	0.19

TABLE III. (Continued).

Energy (eV)	Ion					
	Ga ⁺	Ga ²⁺	Ga ³⁺	In ⁺	In ²⁺	In ³⁺
180	6.14	0.46	0.06	6.86	0.89	0.18
185	6.06	0.45	0.06	6.75	0.88	0.18
190	5.98	0.45	0.07	6.62	0.88	0.18
195	5.87	0.44	0.07	6.51	0.87	0.18
200	5.85	0.45	0.07	6.38	0.86	0.18

high-energy peak. More recent measurements of single ionization by Vainshtein *et al.*⁶ (Figs. 8 and 9) show only low-energy peaks, in agreement with our results, but then fall much faster at higher energies. Shapes measured with the present apparatus have been tested by measuring cross-section shapes for the rare gases² and the CO and CO₂ molecules;²⁶ they agree well with accepted data in the literature.²⁷ It is hard to explain the differences in shape from the available information.

The magnitudes of the cross sections measured in both previous works are much smaller than the present results. We have been unable to identify any systematic error in our apparatus which would produce this large difference. Part of the difference between the present results and those of Vainshtein *et al.*⁶ may be attributed to their use of lead to calibrate their quartz microbalance, the method they used to measure the flux of neutral atoms.^{28,29} We have recently measured the ionization cross section of lead (and of many other atoms),²⁶ and obtain a cross section which is roughly 25% larger than their value. The appropriate correction to their calibration would raise their Ga and In cross sections closer to the present measurements.

One other way to compare the present and previous data is by the ratios of measured In to Ga cross sections. Our ratio of the peak cross sections $\sigma(\text{In}^+)/\sigma(\text{Ga}^+)$ (at about 30 eV) is 1.32, in agreement within the stated errors with the 1.23 ratio of Vainshtein *et al.*⁶

Our double-ionization results and those of Vainshtein *et al.*⁶ agree very well with each other. This is surprising, since our values for total and single ionization differ so greatly. An interesting detail we both observe is a difference between the Ga and In double-ionization shapes; the In²⁺ cross section peaks near 100 eV while Ga²⁺ continues to rise up to 200 eV.

Another comparison can be made to the cross section for single ionization of Sb²⁺,²⁴ which is isoelectronic with In. The measured value for Sb²⁺ is included in Fig. 8, scaled in magnitude by the ratio of the squares of the ionization potentials, $(25.3/5.79)^2$, and scaled along the energy axis so that its threshold matches that of In. The scaled Sb²⁺ cross section is roughly twice as large, due in part because 4*d* ionization leads only to single ionization of Sb²⁺ and only to double ionization of In.²⁴

The peak cross section for single ionization of the isonuclear ion Ga⁺ is measured³⁰ to be 0.92 Å², only 0.100 times that of neutral Ga. This agrees fairly well with the ratio of the squares of the ionization potentials $(6.00/20.51)^2=0.086$.

C. Comparison to theory

Several classical or semiempirical methods are commonly used to estimate unmeasured ionization cross sections. Measurements of the Ga and In atoms provide good tests of these calculations in a part of the Periodic

TABLE IV. Orbital ionization energies for Ga and In.

Atom	Photoelectron spectra				Photoabsorption		Theory		Used in this work
	Ref. 23	Ref. 36	Ref. 37	Ref. 38	Ref. 22	Ref. 39	Ref. 33		
Ga 4 <i>p</i>		6.00				5.67	6.00	6.00	
4 <i>s</i> (triplet)		12.0				11.55	11	12.0	
4 <i>s</i> (singlet)		14.8						14.8	
3 <i>d</i>				22	27–29	32.46	20.5	27.5	
3 <i>p</i>				109		121.9	109	109	
3 <i>s</i>				162			162	162	
In 5 <i>p</i>	5.78		5.8			5.36	5.79	5.78	
5 <i>s</i> (triplet)	11.1		11.1			10.13	10	11.1	
5 <i>s</i> (singlet)	13.6							13.6	
4 <i>d</i>	25–26			20		28.9	20.5	25.5	
4 <i>p</i>				81			95.39	86	
4 <i>s</i>				126		135.4	126	126	

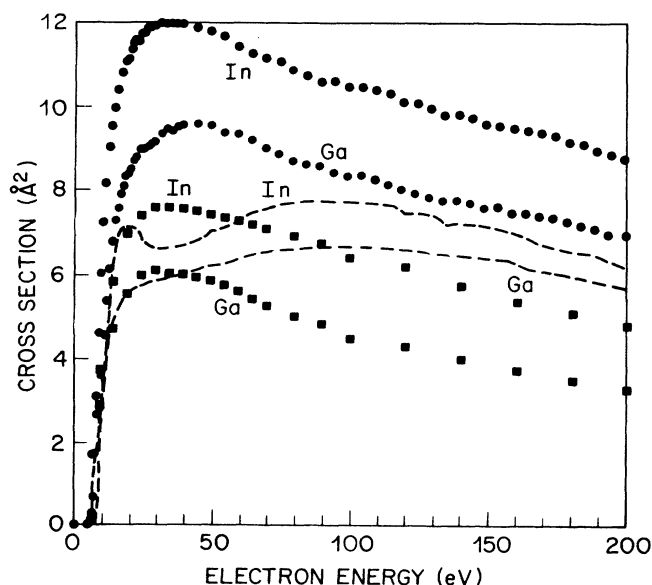


FIG. 7. Comparison of the measured total-ionization cross sections for Ga and In (●) to the measurements of Refs. 4 and 5 (---) and Ref. 6 (■).

Table where there has been very little data.

Comparisons of experiment to calculations according to Gryzinski,³¹ Lotz,^{32,33} and Mann³⁴ for single ionization are shown in Figs. 8 and 9. For the Gryzinski and Lotz calculations, we have used orbital ionization energies from the recent literature, as listed in Table IV. Ioniza-

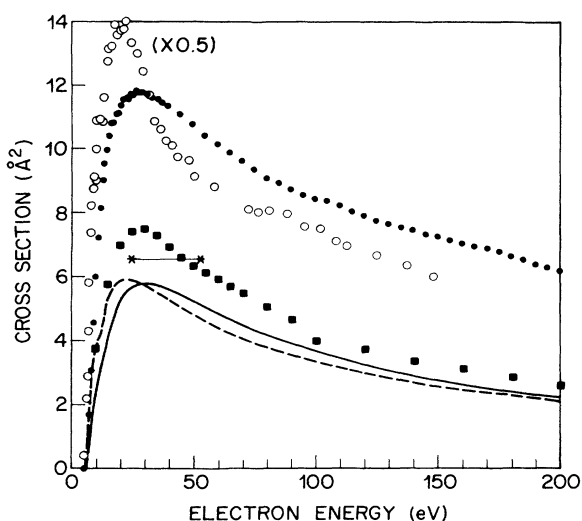


FIG. 8. Comparison of the measured single-ionization cross sections for In (●) to the calculations of Gryzinski (—), Lotz (---), and Mann (*—*). Mann calculates the maximum cross section but does not identify the corresponding energy. Also shown are the measured cross sections of Vainshtein *et al.* (■), and the scaled measured cross section for ionization of the isoelectronic ion Sb^{2+} (○).

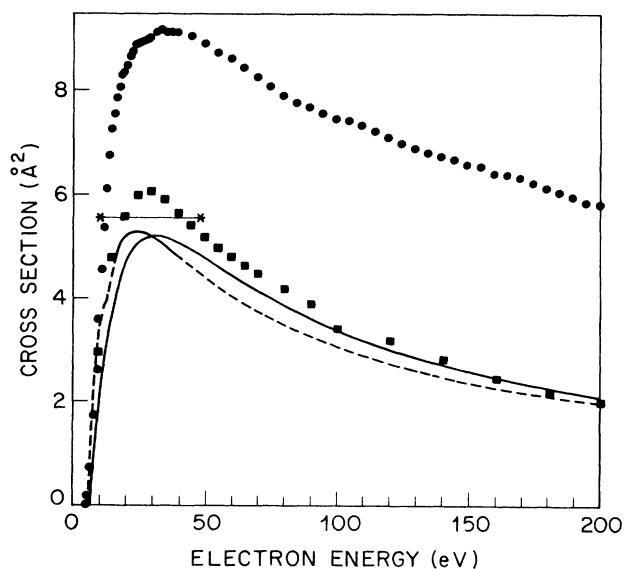


FIG. 9. Comparison of the measured single-ionization cross sections for Ga (●) to the calculations of Gryzinski (—), Lotz (---), and Mann (*—*). Mann calculates the maximum cross section but does not identify the corresponding energy. Also shown is the measured cross section of Vainshtein *et al.* (■).

tion from the $3d$ and $4d$ orbitals of Ga and In, respectively, is omitted, since the ionization energies of electrons from these orbitals lie above the double-ionization energies. Thus, single ionization is calculated from the outermost p and s electrons only. McGuire's calculations³⁵ are not directly applicable to Ga and In since the low-ionization energies of the $4p$ and $5p$ electrons, respectively, lie below the range of validity of his parameters.

We see that although the Gryzinski, Lotz, and Mann values agree with each other, they are nearly a factor of 2 smaller than experiment. Part of the difference may be that indirect ionization is omitted from these theories. A similar difference was found also for ionization of Ga^+ .³⁰ All of these calculations predict the ratio of In to Ga cross sections considerably better. Gryzinski and Lotz predict that the magnitude of the In peak cross sections exceeds that of Ga by about 11%, while Mann's prediction of 32% agrees with the measured 32%. The peak position of Gryzinski agrees best with experiment.

Since the $3d$ and $4d$ ionization energies of Ga and In, respectively, lie above the double-ionization potentials and below the triple-ionization potentials, ionization of this inner orbital should lead primarily to double ionization and should give a lower limit to the double-ionization cross sections. Contributions from direct double ionization and excitation ionization should also contribute, but are not expected to be as large. Figures 10 and 11 compare our measured double-ionization cross sections to the d -shell ionization cross sections calculated according to Gryzinski, Lotz, and McGuire, using the experimental orbital energies from Table IV. The agree-

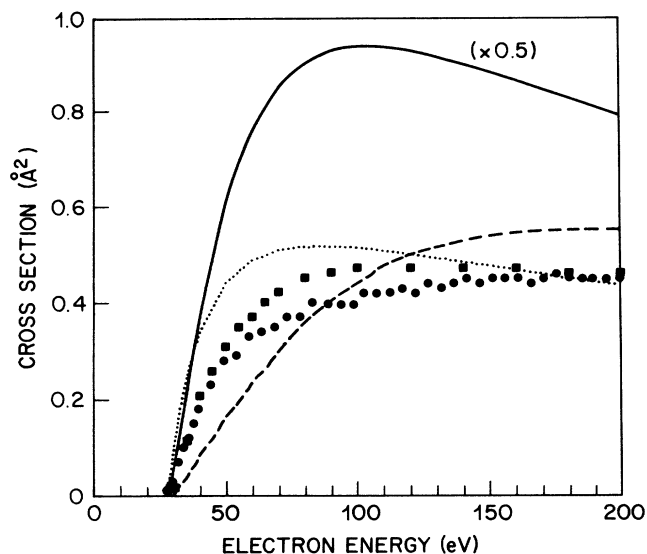


FIG. 10. Comparison of the measured double-ionization cross sections for Ga (●) this work, and (■) Vainshtein *et al.*, to the calculations of Gryzinski (—), Lotz (· · · ·), and McGuire (— —) for ionization from the $3d$ orbital.

ment in magnitude is best for the Lotz calculations. The Gryzinski calculations of the d -shell cross sections are two and four times larger than measured double ionization. The McGuire calculation for Ga comes close to experiment, but the In calculation is twice as large. Although the quantitative agreement is not very good, the general agreement of all these calculations with experiment suggests that d -electron ionization is a major route to double ionization of Ga and In.

V. CONCLUSIONS

The Ga and In atoms are ideal candidates for cross-section measurements by the fast-beam method since their ground states are isolated from all excited states and they have no known metastable states. Thus, it is easy to verify that the neutral beams are entirely in their ground states. Even though their ionization potentials are low (~ 6 eV), and therefore not energy resonant with triethylamine, charge-transfer neutralization takes place readily, probably through metastable states of the ions which can be neutralized directly to the ground state.

The shapes of the single-ionization cross sections are similar to those of many other atoms, with single-

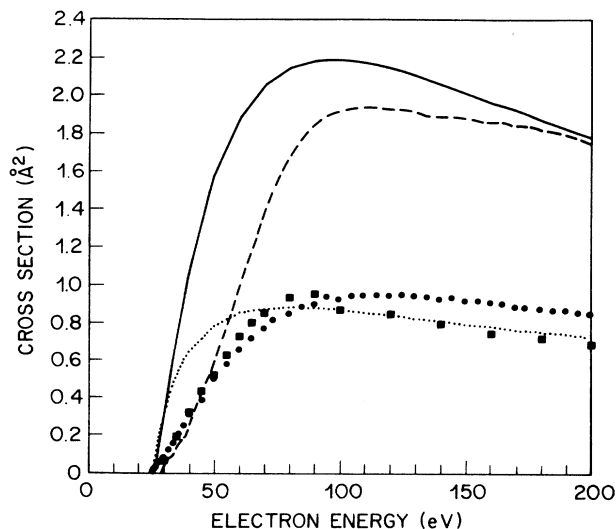


FIG. 11. Comparison of the measured double-ionization cross sections for In (●) this work, and (■) Vainshtein *et al.*, to the calculations of Gryzinski (—), Lotz (· · · ·), and McGuire (— —) for ionization from the $4d$ orbital.

ionization peaks close to the classically predicted energy of four times threshold. Indirect ionization is observed near threshold and above about 100 eV. The measured single-ionization and derived total-ionization cross sections disagree substantially with those from the only previous measurements. Double ionization appears to have major contributions from ionization of the $3d$ and $4d$ electrons of Ga and In, respectively.

The commonly used approximate formulas of Gryzinski, Lotz, and Mann predict some features of the cross sections, but no one formula adequately describes all of the measurements. They all predict the absolute cross section for single ionization to be too small by nearly a factor of 2, but predict the $\sigma(\text{In})/\sigma(\text{Ga})$ ratio more accurately.

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¹Electron Impact Ionization, edited by T. D. Märk and G. H. Dunn (Springer, New York, 1985).

²R. C. Wetzel, F. A. Baiocchi, T. R. Hayes, and R. S. Freund, Phys. Rev. A **35**, 559 (1987).

³T. R. Hayes, R. C. Wetzel, and R. S. Freund, Phys. Rev. A **35**, 578 (1987).

⁴L. L. Shimon, E. I. Nepipov, and I. P. Zapesochnyi, Zh. Tekh.

Fig. **45**, 688 (1975) [Sov. Phys. Tech. Phys. **20**, 434 (1975)].

⁵I. P. Zapesochnyi, J. E. Kontros, and L. L. Shimon, in *Proceedings of the Ninth International Conference on the Physics of Electronic and Atomic Collisions, Seattle, 1975*, edited by J. S. Risley and R. Geballe (University of Washington, Seattle, 1975), p. 900.

⁶L. A. Vainshtein, D. G. Golovach, V. I. Ochkur, V. I.

- Rakhovskii, N. M. Romyantsev, and V. M. Shustryakov, *Zh. Eksp. Teor. Fiz.* **93**, 65 (1987) [*Sov. Phys.—JETP* **66**, 36 (1987)].
- ⁷T. R. Hayes, R. J. Shul, F. A. Baiocchi, R. C. Wetzel, and R. S. Freund, *J. Chem. Phys.* **89**, 4035 (1988).
- ⁸Colutron Research Corp., Boulder, CO 80301; L. Wahlin, *Nucl. Instrum. Methods* **27**, 55 (1964).
- ⁹D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.* **97**, 4136 (1975).
- ¹⁰C. Utsunomiya, T. Kobayashi, and S. Nagakura, *Chem. Phys. Lett.* **39**, 245 (1976).
- ¹¹T. R. Hayes, R. C. Wetzel, F. A. Baiocchi, and R. S. Freund, *J. Chem. Phys.* **88**, 823 (1988).
- ¹²C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1958), Vol. III.
- ¹³C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1952), Vol. II.
- ¹⁴G. H. Dunn, in *Electron Impact Ionization*, edited by T. D. Märk and G. H. Dunn (Springer, New York, 1985).
- ¹⁵R. E. Walstedt and R. F. Bell, *J. Chem. Phys.* **87**, 1423 (1987).
- ¹⁶B. Cabaud, A. Hoareau, P. Noonou, and R. Uzan, *Int. J. Mass. Spectrom. Ion Phys.* **8**, 181 (1972).
- ¹⁷J. P. Connerade and M. A. Baig, *J. Phys. B* **14**, 29 (1981).
- ¹⁸M. G. Kozlov and G. P. Startsev, *Opt. Spektrosk.* **24**, 8 (1968) [*Opt. Spectrosc. (USSR)* **24**, 3 (1968)].
- ¹⁹C. D. Caldwell, M. O. Krause, and J. Jimenez-Mier, *Phys. Rev. A* **37**, 2408 (1988).
- ²⁰J. P. Connerade and M. A. Baig, *J. Phys. B* **15**, L587 (1982).
- ²¹B. E. Krylov and M. G. Kozlov, *Opt. Spektrosk.* **47**, 1044 (1979) [*Opt. Spectrosc. (USSR)* **47**, 579 (1979)].
- ²²J. P. Connerade, *Proc. R. Soc. London, Ser. A* **354**, 511 (1977).
- ²³E. P. F. Lee and A. W. Potts, *J. Electron Spectrosc. Relat. Phenom.* **19**, 65 (1980).
- ²⁴A. Müller, K. Tinschert, Ch. Achenback, E. Salzborn, R. Becker, and M. S. Pindzola, *Phys. Rev. Lett.* **54**, 414 (1985).
- ²⁵S. M. Younger, *Phys. Rev. A* **35**, 4567 (1987).
- ²⁶R. S. Freund, R. c. Wetzel, and R. J. Shul (unpublished).
- ²⁷D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).
- ²⁸D. G. Golovach, V. I. Rakhovskii, and V. M. Shustryakov, *Prib. Tekh. Eksp.* **6**, 141 (1986) [*Instrum. Exp. Tech. (USSR)* **29**, 1396 (1986)].
- ²⁹S. I. Pavlov and G. I. Stotskii, *Zh. Eksp. Teor. Fiz.* **58**, 108 (1970) [*Sov. Phys.—JETP* **31**, 61 (1970)].
- ³⁰W. T. Rogers, G. Stefani, R. Camilloni, G. H. Dunn, A. Z. Msezane, and R. J. W. Henry, *Phys. Rev. A* **25**, 737 (1982).
- ³¹M. Gryzinski, *Phys. Rev.* **138**, A336 (1965).
- ³²W. Lotz, *Z. Phys.* **232**, 101 (1970).
- ³³W. Lotz, *J. Opt. Soc. Am.* **60**, 206 (1970).
- ³⁴J. B. Mann, *J. Chem. Phys.* **46**, 1646 (1967).
- ³⁵E. J. McGuire, *Phys. Rev. A* **16**, 62, (1977); **16**, 73 (1977); **20**, 445 (1979).
- ³⁶M. O. Krause, A. Svensson, A. Fahlman, and T. A. Carlson, *Z. Phys. D* **2**, 327 (1986).
- ³⁷B. Ruscic, G. L. Goodman, and J. Berkowitz, *J. Electron Spectrosc. Relat. Phenom.* **41**, 357 (1986).
- ³⁸K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergman, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *ESCA Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy*, (Almqvist & Wiksells, Boktryckeri AB, 1967), Appendix 1.
- ³⁹E. Clementi, *At. Data Nucl. Data Tables* **14**, 177 (1974).

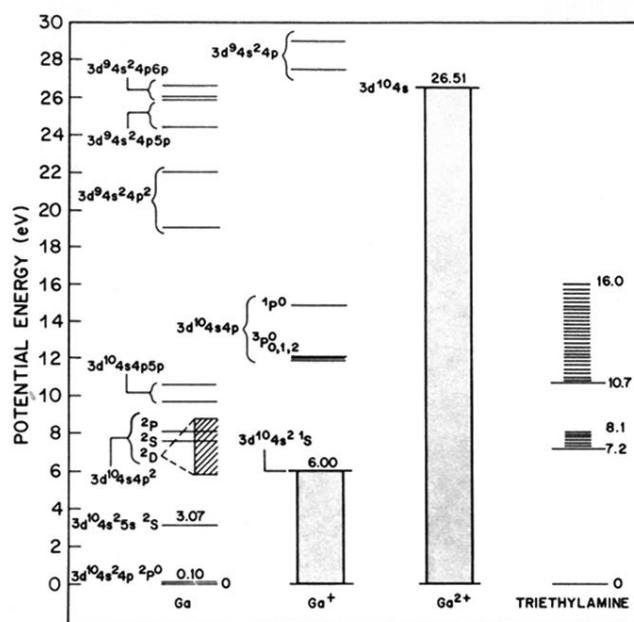


FIG. 1. Potential-energy diagram showing the electronic states and near-resonant charge-transfer neutralization of Ga^+ by triethylamine.

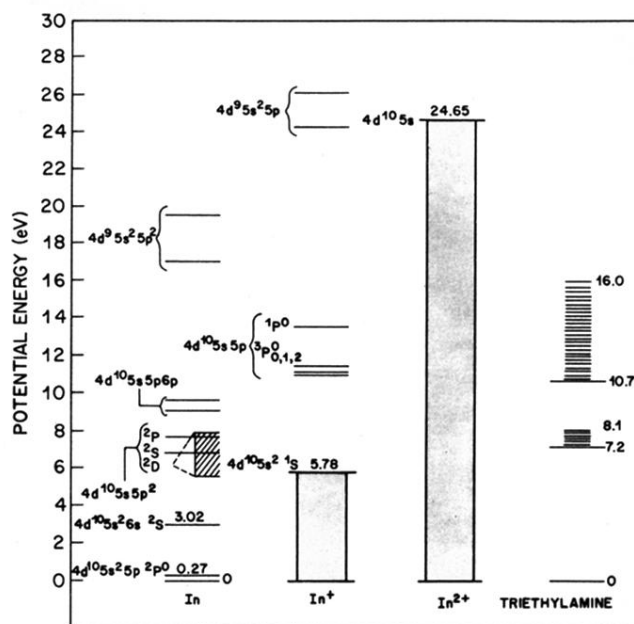


FIG. 2. Potential-energy diagram showing the electronic states and near-resonant charge-transfer neutralization of In^+ by triethylamine.