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Electron-impact ionization of multicharged metal ions: Ni^{3+}, Cu^{2+}, Cu^{3+}, and Sb^{3+}

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Absolute electron-impact ionization cross sections were measured as a function of collision energy for the multicharged metallic ions Ni^{3+}, Cu^{2+}, Cu^{3+}, and Sb^{3+}. The measurements cover an energy range from below threshold to 1000 eV (1500 eV for Cu^{2+}). Recent distorted-wave direct ionization calculations agree with the measurements for Ni^{3+}, Cu^{2+}, and Cu^{3+} within 20%. Inner-shell excitation followed by autoionization produces up to a factor-of-2 enhancement in the Sb^{3+} cross section, and a rapid decrease in this indirect contribution at higher energies indicates the dominance of dipole-forbidden excitations.

I. INTRODUCTION

Electron-impact ionization is one of the primary atomic processes important to our understanding of laboratory plasmas, especially for the interpretation of diagnostic data and for the modeling of power balance in tokamaks and other controlled thermonuclear research devices. Plasma conditions near the edge of such devices have received considerable attention in recent years, and quantitative information about the low charge states of common impurity ions is needed.[1] The most likely heavy impurities in such plasmas are metallic ions from walls, limiters, and other structures in the device.

The relative importance of indirect ionization varies widely in previous ionization studies on metallic ions. Ti^{2+} and Ti^{3+} are dominated[2,3] by indirect ionization, while Fe^{2+} does not exhibit predicted[4] enhancements. Na-like metal ions have significant indirect ionization contributions,[5] in reasonable agreement with detailed calculations.[6] Despite the growing data bases of experiment and theory, however, it is still difficult to even qualitatively predict the cross section for ionization of a particular ion.

The target ions in the current study were selected for comparison with previous specific calculations and for immediate application in fusion research. Cu and Ni are probable contaminants in fusion devices; no previous data are available for multicharged ions of these elements. Sb^{3+} was measured to test predictions[7] of unusual and dominant indirect ionization contributions and to extend previous isonuclear measurements on Sb^{+} and Sb^{2+} by Müller *et al.*[8]

II. EXPERIMENTAL TECHNIQUE

The measurements utilized crossed beams of ions from the Oak Ridge National Laboratory—PIG multicharged ion source[9] and magnetically confined electrons from a gun similar to that described by Taylor *et al.*[10] The metal ions were created by chlorination of metal inserted into the ion-source discharge region.[3] The ions were then accelerated through a potential of 10 kV and formed into a beam, which was transported into an ultrahigh vacuum chamber and electrostatically analyzed at 90° to remove ions that changed charge during the flight from the ion source. After crossing the electron beam, the ions were electrostatically analyzed to separate ionized ions from the parent ion beam. Signal events were detected by counting those target ions which lost one electron in the interaction region, and the electron beam was chopped to allow separation of signal events from background. Beam profiles and overlap, detector efficiency, and total beam currents were measured to allow the determination of absolute cross sections. The total absolute uncertainty of these measurements at good confidence level for a typical energy near the peak cross section, including statistics at the two-standard-deviation level, is ±8%. Uncertainties reported in the data table (Table I) reflect one-standard-deviation relative uncertainty only. Additional experimental details are available in recent publications.[5,11]

III. RESULTS

A. Ni^{3+}

The only published cross-section measurement for a Ni ion is the recent work of Montague and Harrison[12] for Ni^{+}. No significant indirect ionization was observed in that measurement, and although some metastable content was found in the incident ion beam, it was not thought to have an appreciable effect on the results. In that case, the semiempirical Lotz formula[13] greatly overestimates the experimental cross section, and the scaled plane-wave Born approximation (PWBA) results of McGuire[14] are generally in good agreement with the experiment.

The cross sections for single ionization of Ni^{3+} as a function of energy are listed in Table I and plotted in Fig. 1. The data are compared to predictions of the semiempirical three-parameter Lotz formula[13] and to distorted-wave (DW) calculations for direct ionization.[15] Both calculations are based on predictions that all target ions are in the ground state and that only the outer-subshell ($3d^7$) electrons and an average of $\frac{3}{4}$ of the electrons in the next inner subshell ($3p^6$) will contribute to single ionization.[15] The removal of a more tightly bound electron will lead to further ionization as the resulting

TABLE I. Cross sections for electron-impact single ionization of Ni^{3+}, Cu^{2+}, Cu^{3+}, and Sb^{3+}. Quoted uncertainties are one-standard-deviation relative only; the total absolute uncertainty for each data set is ±8% near the peak cross section at good confidence level (equivalent to two standard deviations for statistical uncertainties).

<table>
<tr><th rowspan="2">Energy (eV) \ Ground-state ionization threshold (eV)</th><th colspan="5">Cross section (10^{-18} cm^2)</th></tr>
<tr><th>Ni^{3+} 54.9</th><th colspan="2">Cu^{2+} 36.8</th><th>Cu^{3+} 55.2</th><th>Sb^{3+} 41.6</th></tr>
<tr><td>25.8</td><td></td><td colspan="2">0.38±0.29</td><td></td><td></td></tr>
<tr><td>26.7</td><td></td><td colspan="2"></td><td>−0.02±0.27</td><td></td></tr>
<tr><td>27.8</td><td></td><td colspan="2">0.42±0.34</td><td></td><td></td></tr>
<tr><td></td><td></td><td>Low metastable content</td><td>High metastable content</td><td></td><td></td></tr>
<tr><td>30.8</td><td></td><td>0.51±0.89</td><td>2.80±0.24</td><td></td><td></td></tr>
<tr><td>31.7</td><td></td><td></td><td></td><td>0.36±0.27</td><td></td></tr>
<tr><td>35.8</td><td></td><td>4.32±1.00</td><td>9.77±0.47</td><td></td><td></td></tr>
<tr><td>36.6</td><td>0.24±1.17</td><td></td><td></td><td>0.15±0.21</td><td>−0.2 ±1.3</td></tr>
<tr><td>39.5</td><td></td><td></td><td></td><td></td><td>0.45±1.6</td></tr>
<tr><td>40.7</td><td></td><td>9.31±1.07</td><td>13.54±0.37</td><td></td><td></td></tr>
<tr><td>41.6</td><td>−0.75±1.07</td><td></td><td></td><td>0.65±0.33</td><td></td></tr>
<tr><td>43.1</td><td></td><td></td><td></td><td></td><td>3.4 ±1.9</td></tr>
<tr><td>45.7</td><td></td><td>14.0 ±1.5</td><td>20.3 ±0.6</td><td></td><td></td></tr>
<tr><td>46.4</td><td>0.89±0.46</td><td></td><td></td><td>1.19±0.17</td><td>10.8 ±1.1</td></tr>
<tr><td>49.6</td><td></td><td></td><td></td><td>1.48±0.34</td><td>23.0 ±1.5</td></tr>
<tr><td>50.5</td><td></td><td>19.2 ±1.0</td><td>23.6 ±0.4</td><td></td><td></td></tr>
<tr><td>51.3</td><td></td><td></td><td></td><td></td><td>30.4 ±1.8</td></tr>
<tr><td>53.2</td><td></td><td></td><td></td><td>1.32±0.40</td><td>34.9 ±1.6</td></tr>
<tr><td>55.4</td><td></td><td>22.3 ±0.9</td><td>24.8 ±0.5</td><td></td><td></td></tr>
<tr><td>56.3</td><td>4.00±0.57</td><td></td><td></td><td>2.53±0.21</td><td>42.3 ±1.1</td></tr>
<tr><td>59.3</td><td>5.73±0.69</td><td></td><td></td><td></td><td>50.7 ±1.0</td></tr>
<tr><td>60.2</td><td></td><td colspan="2">27.7±0.4</td><td>4.79±0.45</td><td></td></tr>
<tr><td>61.2</td><td></td><td colspan="2"></td><td></td><td>53.8 ±1.6</td></tr>
<tr><td>62.8</td><td>9.03±0.56</td><td colspan="2"></td><td></td><td>56.4 ±1.0</td></tr>
<tr><td>63.2</td><td></td><td colspan="2"></td><td>5.11±0.37</td><td></td></tr>
<tr><td>65.4</td><td></td><td colspan="2">29.3±0.4</td><td></td><td></td></tr>
<tr><td>66.3</td><td>11.5 ±0.46</td><td colspan="2"></td><td>6.62±0.35</td><td>59.7 ±1.0</td></tr>
<tr><td>69.4</td><td></td><td colspan="2"></td><td></td><td>62.4 ±1.0</td></tr>
<tr><td>70.3</td><td></td><td colspan="2">31.5±0.4</td><td></td><td></td></tr>
<tr><td>71.5</td><td></td><td colspan="2"></td><td>8.57±0.45</td><td></td></tr>
<tr><td>72.8</td><td></td><td colspan="2"></td><td></td><td>64.9 ±1.0</td></tr>
<tr><td>75.1</td><td></td><td colspan="2">33.7±0.4</td><td></td><td></td></tr>
<tr><td>76.1</td><td>15.97±0.79</td><td colspan="2"></td><td>11.14±0.29</td><td>68.4 ±1.0</td></tr>
<tr><td>80.1</td><td></td><td colspan="2">35.5±0.4</td><td></td><td></td></tr>
<tr><td>81.1</td><td></td><td colspan="2"></td><td>12.65±0.52</td><td>73.8 ±1.2</td></tr>
<tr><td>85.1</td><td></td><td colspan="2">36.9±0.5</td><td></td><td></td></tr>
<tr><td>86.1</td><td>18.81±0.65</td><td colspan="2"></td><td>13.24±0.26</td><td>75.6 ±1.0</td></tr>
<tr><td>89.9</td><td></td><td colspan="2">37.1±0.4</td><td></td><td></td></tr>
<tr><td>91.0</td><td></td><td colspan="2"></td><td>15.60±0.45</td><td>77.2 ±1.1</td></tr>
<tr><td>95.1</td><td></td><td colspan="2">38.1±0.2</td><td></td><td></td></tr>
<tr><td>96.0</td><td>21.36±0.45</td><td colspan="2"></td><td>15.9 ±0.2</td><td>76.7 ±1.0</td></tr>
<tr><td>100</td><td></td><td colspan="2">39.2±0.3</td><td></td><td></td></tr>
<tr><td>106</td><td>24.0 ±0.4</td><td colspan="2"></td><td>17.5 ±0.2</td><td>76.3 ±1.0</td></tr>
<tr><td>110</td><td>24.9 ±0.8</td><td colspan="2">40.1±0.4</td><td></td><td></td></tr>
<tr><td>116</td><td></td><td colspan="2"></td><td>19.2 ±0.2</td><td>73.8 ±1.0</td></tr>
<tr><td>120</td><td>25.1 ±1.0</td><td colspan="2">41.9±0.3</td><td>20.4 ±0.4</td><td>72.4 ±1.0</td></tr>
<tr><td>126</td><td></td><td colspan="2"></td><td>20.0 ±0.2</td><td>68.4 ±1.0</td></tr>
<tr><td>131</td><td>27.4 ±0.8</td><td colspan="2"></td><td></td><td></td></tr>
<tr><td>136</td><td></td><td colspan="2"></td><td>21.1 ±0.2</td><td>65.5 ±1.0</td></tr>
</table>

TABLE I. (*Continued*).

	Cross section (10^{-18} cm^2)			
Energy (eV) \ Ground-state ionization threshold (eV)	Ni^{3+} 54.9	Cu^{2+} 36.8	Cu^{3+} 55.2	Sb^{3+} 41.6
145	28.3 ±0.4	43.9±0.6	22.1 ±0.2	64.1 ±1.0
155			22.9 ±0.2	60.4 ±1.0
160	31.0 ±0.7			
170	28.4 ±1.1	45.4±0.5	24.4 ±0.3	
175	30.2 ±0.6		24.2 ±0.3	59.8 ±1.0
195	30.4 ±0.3	46.5±0.4	25.7 ±0.3	58.3 ±1.0
218		45.1±0.4	26.7 ±0.1	
220	31.4 ±0.9			58.0 ±1.0
244	31.5 ±0.2	43.4±0.4	27.2 ±0.2	56.8 ±1.0
268	32.1 ±0.2	48.8±0.3	27.5 ±0.1	55.6 ±1.0
293	31.7 ±0.2	43.7±0.2	27.6 ±0.6	54.0 ±1.0
339		42.4±0.3		
343	30.9 ±0.2		27.6 ±0.4	51.5 ±1.0
391	30.0 ±0.2	39.9±0.2	27.0 ±0.2	48.7 ±1.0
439		37.0±0.2		
442	30.1 ±0.3		26.4 ±0.2	48.0 ±1.0
491	28.9 ±0.2	35.4±0.2	25.9 ±0.1	45.3 ±1.0
590	28.4 ±0.4	33.5±0.1	23.8 ±0.2	40.4 ±1.0
687		31.7±0.3		
691	26.4 ±0.9		22.9 ±0.2	37.3 ±1.0
835		29.1±0.1		
840	24.2 ±0.6		21.6 ±0.3	34.7 ±1.0
986		26.1±0.1		
991	22.1 ±0.6		20.1 ±0.2	31.3 ±1.0
1233		23.6±0.2		
1480		22.1±0.1		

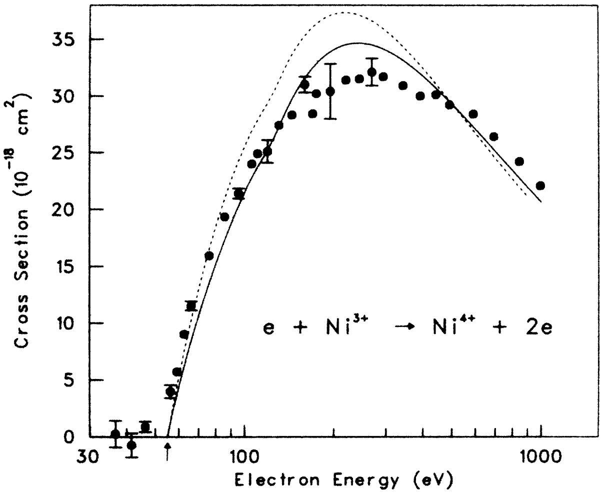

FIG. 1. Electron-impact ionization of Ni^{3+}. Typical relative uncertainties at the one-standard-deviation level are shown, and the absolute uncertainty at good confidence level is shown near 200 eV. Curves are from the three-parameter semiempirical Lotz formula (Ref. 13, dashed line) and DW calculations (Ref. 15, solid line). Both calculations assume contributions from direct ionization of $3d^7$ electrons and from $\frac{3}{4}$ of the $3p^6$ subshell. The arrow marks the 54.9-eV threshold for ionization of ground-state ions.

core-excited ion autoionizes, and in fact $\frac{1}{4}$ of the levels associated with the $3p^5 3d^7$ configuration are predicted to autoionize. The observed onset of ionization is near the 54.9-eV threshold[16] for removal of an electron from the ground-state ion; we conclude that there is little, if any, metastable component in the ion beam. With minor discrepancies in some energy ranges, the DW calculations reproduce the data well, and the Lotz prediction is only slightly less accurate, although both appear to slightly underestimate the cross section at high energies. In this case the PWBA results taken from McGuire's published curve[17] is a factor of 2 lower than the experiment. No indications of significant indirect ionization, such as the discontinuities characteristic of excitation autoionization, are apparent in the data.

B. Cu^{2+} and Cu^{3+}

Tabulated cross sections are listed in Table I and the data are plotted in Figs. 2 (Cu^{2+}) and 3 (Cu^{3+}). The data are compared to the predictions of the three-parameter Lotz formula[13] and to distorted-wave calculations[15] for direct ionization of ground-state outer-subshell $3d$ electrons in each case. For Cu^{+}, the calculations include $\frac{2}{3}$ of the ionization expected from the inner $3p^6$ subshell; for Cu^{2+}, all levels of the $3p^5 3d^9$ configuration resulting

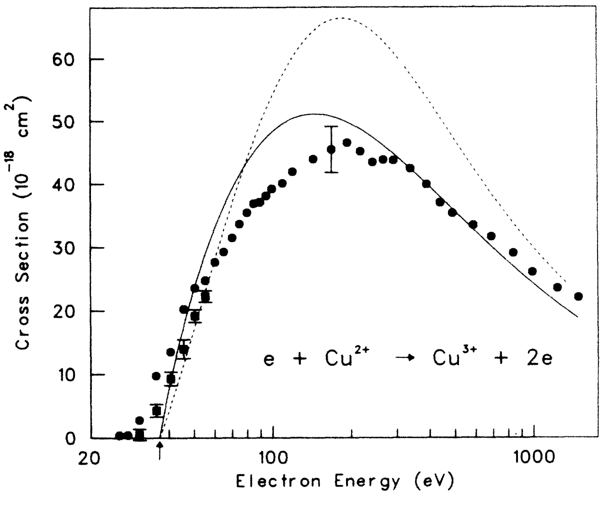

FIG. 2. Electron-impact ionization of Cu^{2+}. The circles and squares represent different metastable contents in the incident ion beam. Relative uncertainties for the high-metastable data are smaller than the plotted points, and a typical absolute uncertainty at good confidence level is shown near 200 eV. Curves are from the semiempirical three-parameter Lotz formula (Ref. 13, dashed curve) and DW calculations (Ref. 15, solid curve) for direct ionization of outer-subshell $3d^9$ electrons. The arrow marks the threshold for ionization of ground-state ions.

from the removal of an inner electron are predicted[15] to autoionize and so result in net double ionization. The observed cross-section thresholds at about 28 eV for Cu^{2+} and at 40 eV for Cu^{3+} are well below the thresholds[16] for ionization of ground-state ions (36.8 and 55.2 eV, respectively). We attribute this to the presence of metastable components in the parent ion beams. The metastable content of the Cu^{2+} was observed to vary from day to day, and two sets of near-threshold data are shown with different metastable fractions. Above 55 eV the two data sets are indistinguishable.

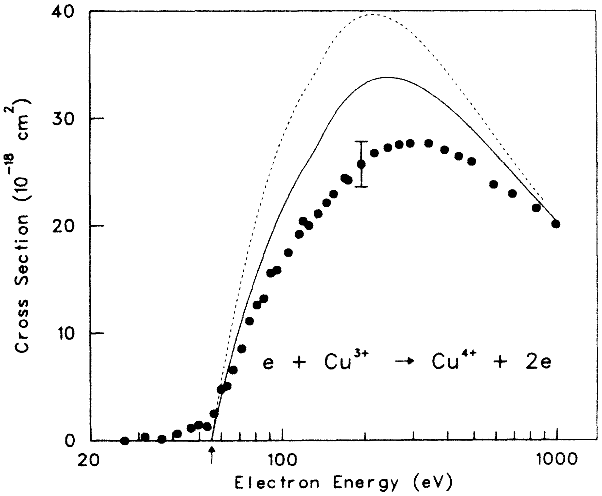

FIG. 3. Electron-impact ionization of Cu^{3+}. Relative uncertainties are smaller than the plotted points, and the absolute uncertainty at good confidence level is shown at 200 eV. Curves are from the semiempirical three-parameter Lotz formula (Ref. 13, dashed curve) and DW calculations (Ref. 15, solid curve) for direct ionization of $3d^8$ electrons and $\frac{2}{3}$ of the $3p^6$ subshell. The arrow marks the ionization threshold for ground-state ions.

The approximate metastable population of the ion beam may be inferred from the shape of the cross-section curve in the near-threshold energy range in cases where the observed threshold is well below that of a ground-state ion, and assuming similar energy dependences for ionization from the ground and metastable states (justified by, for instance, the success of empirical scaling laws for ionization such as the Lotz formula[13]). Although the Cu^{3+} experimental onset is observed near 40 eV, the cross section remains small until the threshold for ionization of ground-state ions, indicating that the metastable ions form a small percentage of the total beam and are well separated in energy from the ground state.

In both cases, the three-parameter Lotz prediction overestimates the peak cross section by about 50%, converging to the experimental values at high energies. DW calculations are in somewhat better agreement with experiments up to the peak cross sections. In each case, distorted-wave results peak at a higher energy than the experiment, but good agreement is found at high energies. Lotz and DW calculations are based on direct ionization of ground-state ions. As in the case of Ni^{3+}, no significant indirect ionization is apparent in either case. No previous electron-impact ionization measurements are found in the literature for any Cu ion.

C. Sb^{3+}

In contrast to the measurements reported above, the cross section for ionization of Sb^{3+} clearly exhibits contributions from indirect ionization. In addition, the major contribution to the peak direct-ionization cross section is due to removal of $4d^{10}$ inner-shell electrons. The dominance of inner-shell ionization in the direct single-ionization process suggests that strong indirect-ionization contributions might be expected from excitation of inner-shell electrons followed by autoionization. Since no DW calculations are available for the direct portion of the ionization, the measurements are compared in Fig. 4 to Lotz one-parameter predictions[18] for ionization of ground-state $4d^{10}5s^2$ electrons. Comparison of direct ionization with theory at low energies is impossible due to the large indirect component, but the high-energy behavior (above 200 eV) suggests that the Lotz prediction is a reasonable estimate of the direct-ionization cross section, probably underestimating it by 20% near the peak cross section.

Previous measurements[8] for single ionization of Sb^{+} and Sb^{2+} show that indirect-ionization contributions near threshold become increasingly important with increasing charge. This trend continues with the present results, where about half of the peak cross section for ionization of Sb^{3+} is attributed to excitation of $4d$ electrons to excited states which autoionize. The rapid increase in cross section which characterizes this process for ions is followed in this case by a rapid decrease in cross section at energies from 90 to 160 eV. This decrease is even more

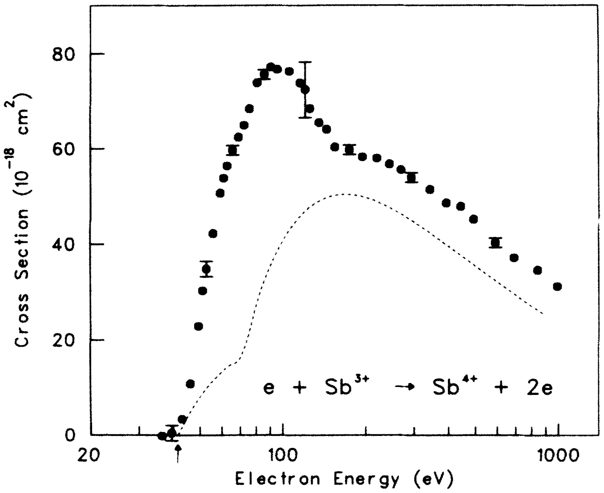

FIG. 4. Electron-impact ionization of Sb^{3+}. Typical relative uncertainties are shown at the one-standard-deviation level and the absolute uncertainty is shown at 100 eV at good confidence level. The dashed curve is a one-parameter Lotz prediction (Ref. 18) for ionization of $4d^{10}$ or $5s^2$ electrons. The arrow indicates the calculated threshold for ionization of ground-state ions.

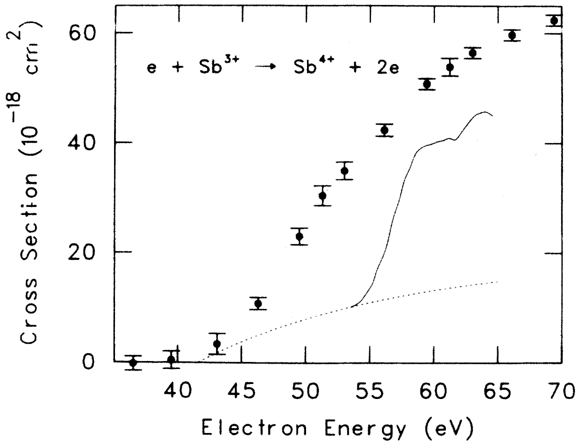

FIG. 5. Electron-impact ionization of Sb^{3+} near threshold. The solid points are the present data; the dashed curve is an estimate of the direct-ionization contribution from $5s^2$ outer electrons (semiempirical Lotz formula, Ref. 18). The solid curve is the predicted excitation-autoionization contribution due to $4d^{10}5s^2 \rightarrow 4d^9 5s^2 nf$ ($n=4,5$) transitions (Ref. 7) added to the Lotz curve.

dramatic considering that the direct component of the cross section is increasing over this energy range. Specific DW calculations of excitation autoionization for this system by Pindzola *et al.*[7] over the energy range 55—65 eV are compared to the present data in Fig. 5; the calculations appear to account for most of the indirect contribution in that limited energy range. These calculations included excitations of the type $4d^{10}5s^2 \rightarrow 4d^9 5s^2 nf$ ($n=4,5$) which then autoionize. Since these transitions are dominated by non-dipole-allowed components, the indirect cross section at higher energies would exhibit the rapid decrease which is observed. Additional similar transitions involving $4d$ electrons excited to higher nf levels ($n=6,7,\ldots$) are also predicted to contribute significantly to the total cross section at energies in the 65—71-eV energy range. The enhancement of the cross section over the direct-ionization contribution between the calculated 41.6-eV threshold[7] and 55 eV is probably a combination of excitation autoionization involving $4d \rightarrow 5d$ transitions[4] and resonant-recombination double autoionization ($4d \rightarrow 4f$ excitation accompanied by capture of the incoming electron, followed by autoionization of two electrons from the resulting highly excited system). Sample calculations[19] predict that resonant-recombination double autoionization is significant in this energy range although complete calculations for all possible transitions have not been performed. A similar "humplike" feature was also observed[11] in ionization of Xe^{3+}; in that case, extensive DW calculations including excitation-autoionization contributions could account for practically the entire experimental cross section.

IV. CONCLUSIONS

The cross sections for electron-impact single ionization of four metallic ions have been presented. No significant indirect-ionization contributions are observed for Cu^{2+}, Cu^{3+}, or Ni^{3+}, and good agreement is found in these cases with DW calculations of direct ionization. For Sb^{3+}, a humplike feature is observed in the near-threshold energy range which is attributed to predominantly non-dipole-allowed excitations of the type $4d \rightarrow nf$ followed by autoionization. Predictions of the Lotz formula are in reasonable agreement with the Sb^{3+} data at high energies, where the indirect ionization no longer contributes significantly.

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[1] See, for example, M. F. A. Harrison, in *Atomic and Molecular Physics of Controlled Thermonuclear Fusion,* Vol. 101 of NATO Advanced Science Institute Series B: Physics, edited by Charles J. Joachain and Douglass E. Post (Plenum, New York, 1983), pp. 441—476.

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