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## Bragg-Rule Applicability to Stopping Cross Sections of Gases for $\alpha$ Particles of Energy 0.3–2.0 MeV\*

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The additivity of atomic stopping cross sections, Bragg's rule, is tested for  $\alpha$  particles in the gaseous compounds H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> (propylene), and (CH<sub>2</sub>)<sub>3</sub> (cyclopropane). Compounds with single and double bonds are found to obey Bragg's rule. Compounds containing triple-bond structure are found to deviate from Bragg's rule by as much as 12.8%, but an empirical triple-bond correction is made to fit all the data of the present experiment. Evidence is seen for a possible physical-state effect.

### I. INTRODUCTION

The additivity of atomic stopping cross sections, Bragg's rule, was first stated by Bragg and Kleeman<sup>1</sup> in 1905. The stopping power of H<sub>2</sub>O (in gas, liquid, and solid state) for  $\alpha$  particles has been measured by many groups.<sup>2-9</sup> The results obtained by these groups are conflicting, and a consistent statement on Bragg's rule cannot be made from these measurements. The energy loss of  $\alpha$  particles in gases has been measured by four groups.<sup>10-14</sup> Schmieder<sup>10</sup> noticed deviation from Bragg's rule for nitrogen-oxygen compounds, but not for carbon-oxygen or carbon-hydrogen compounds. Park<sup>11</sup> found no deviation from Bragg's rule for hydrocarbons. The measurements by Palmer<sup>12</sup> and by Rotondi,<sup>13</sup> using  $\alpha$  particles of energy 1 MeV or above, also showed no deviation from Bragg's rule. The measurements by Reynolds *et al.*<sup>15</sup> and by Park and Zimmerman<sup>16</sup> for protons in gases, however, indicated a deviation from Bragg's rule below 150 keV. Thus, it might then be expected that deviations would occur for  $\alpha$ -particle energies below 600 keV.

The experimental tests of Bragg's rule mentioned above may be classified broadly into two general categories: (a) physical-state effects (gas, liquid, or solid) and (b) chemical-binding effects. The purpose of the present experiment is to attempt to clarify some of the conflicting results of the above-mentioned experiments by concentrating on chemical-binding effects for gaseous compounds. The goal is to answer two questions: (a) Is Bragg's rule valid for a given class of compounds and a given energy region? (b) If Bragg's rule does not hold, what is the reason for it not holding, and can a correction be made to account for the deviation?

Previous experiments have yielded answers to (a), but none have yielded the answer to (b) explicitly.

The experimental procedure, accuracy, results, and comparison with other measurements for  $\alpha$ -particle stopping cross sections in H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and (CH<sub>2</sub>)<sub>3</sub> for 0.3–2-MeV  $\alpha$  particles are given in a separate paper,<sup>17</sup> which will be referred to as I.

### II. ANALYSIS OF DATA

#### A. Physical State and Chemical Binding

Bragg's rule may be stated as follows:

$$\epsilon(X_m Y_n) = m\epsilon(X) + n\epsilon(Y), \quad (1)$$

where  $\epsilon(X_m Y_n)$  is the stopping cross section  $dE/(Ndx)$  of the molecule  $X_m Y_n$ ,  $N$  is the number of molecules per unit volume,  $\epsilon(X)$  and  $\epsilon(Y)$  are the stopping cross sections of the atomic constituents  $X$  and  $Y$ , respectively. Deviations from (1) may be caused by physical-state effects, as for example, in the molecule CO<sub>2</sub> (a gaseous compound);  $\epsilon(C)$  would usually be obtained from matter in the solid state and  $\epsilon(O)$  from matter in the gaseous state. If the atomic substance is in a physical state different from that of the molecular substance of which it is a constituent, departures from the simple additivity rule may occur, since nothing regarding the physical state is considered in (1). Indeed, physical-state effects have been seen in molecular stopping data, such as the stopping power of H<sub>2</sub>O vapor by Reynolds *et al.*<sup>15</sup> being an average of 11% higher than that of D<sub>2</sub>O ice by Wenzel and Whaling<sup>18</sup> for protons of 30–600-keV energy. Palmer<sup>9</sup> found the stopping power to be higher in the vapor state than in the liquid state for low-energy  $\alpha$  particles in water, ethyl alcohol, and carbon tetrachloride.

TABLE I. Chemical structure of gaseous compounds used in the present analysis as given by Pauling, unless otherwise noted.

| Gas                               | Structure   | Gas              | Structure   |
|-----------------------------------|---|------------------|---|
| CH <sub>4</sub>                   | $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$   | H <sub>2</sub>   | H-H   |
| C <sub>2</sub> H <sub>2</sub>     | $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}\equiv\text{C}-\text{H} \\   \\ \text{H} \end{array}$   | N <sub>2</sub>   | $:\ddot{\text{N}}\equiv\text{N}:$   |
| C <sub>2</sub> H <sub>4</sub>     | $\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{C}=\text{C} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$  | O <sub>2</sub>   | $:\text{O}=\ddot{\text{O}}:$ <sup>a</sup>   |
| C <sub>2</sub> H <sub>6</sub>     | $\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$                        | CO               | $(:\text{C}\equiv\text{O}:^+, :\text{C}=\ddot{\text{O}}:, :\text{C}=\ddot{\text{O}}:, \text{?}\text{C}-\ddot{\text{O}}:)^c$   |
| C <sub>3</sub> H <sub>6</sub>     | $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}=\text{C} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ | N <sub>2</sub> O | $(:\ddot{\text{N}}=\overset{+}{\text{N}}=\ddot{\text{O}}:, \text{?}\ddot{\text{N}}=\overset{+}{\text{N}}-\ddot{\text{O}}:, :\text{N}=\overset{+}{\text{N}}-\ddot{\text{O}}:)^d$ |
| (CH <sub>2</sub> ) <sub>3</sub> H | $\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$                        | NH <sub>3</sub>  | $\text{H}-\overset{+}{\text{N}}-\text{H}$<br>$ $<br>$\text{H}$  |

<sup>a</sup>Given by Orville-Thomas, Ref. 21.

<sup>b</sup>Given by Bent, Ref. 20.

<sup>c</sup>Resonance structures (see text);  $:\text{C}\equiv\text{O}:^+$  has a 60% contribution.

<sup>d</sup>Resonance structures (see text); each structure has a one-third contribution.

A second reason for departure from (1) may be the chemical binding of the atoms in the molecule. Equation (1) inherently assumes that this binding is negligible insofar as the stopping process is concerned. For the gases of the present experiment, the atoms H, C, N, and O are bound together by sharing two, four, or six electrons corresponding, respectively, to single, double, or triple covalent bonds. Table I shows the chemical binding and a reference for the structure given for each gas. The single, double, and triple bonds are represented by one, two, and three straight lines between the atoms, respectively. Any valence electrons not used in binding are represented by dots. The majority of the structures in the table are given by Pauling.<sup>19</sup> The structure of CO<sub>2</sub> is that given by Bent<sup>20</sup> and that of O<sub>2</sub> by Orville-Thomas.<sup>21</sup> For CO and N<sub>2</sub>O Pauling introduces the concept of resonance structure, which simply means that the actual structure is a hybrid of the ones listed, with each structure having a particular weight. For CO Pauling used the experimental knowledge that the CO bond length is intermediate between that expected for a double bond and for a triple bond,

and also that CO has a small dipole moment that is less than it would be if the CO structure were 100% triple bond. By so doing, he determined that the triple-bond structure  $:\text{C}\equiv\text{O}:^+$  makes a 60% contribution to the resonance description of the actual binding.

There has been some criticism of the resonance-structure representation of CO structure. Long and Walsh<sup>22</sup> questioned the resonance representation and suggested a modified double-bond structure; however, the validity of their arguments were questioned by Moffitt.<sup>23</sup> Sahni<sup>24</sup> and Jaffe and Orchin<sup>25</sup> made theoretical molecular-orbital calculations which indicated 100% triple-bond structure for CO. Linnett<sup>26</sup> and Luder<sup>27</sup> have also suggested a triple-bond structure for CO. The empirical correction found in this experiment seems to support in part the resonance structure due to Pauling, and that is why we have only included his structure in Table I.

#### B. Tests of Bragg's Rule

Five tests of Bragg's rule have been made with the experimental measurements of I. The first test was made by substituting the  $\epsilon(\text{C})$  obtained by Chu and Powers<sup>28</sup> from a solid carbon thin film and  $\epsilon(\text{O}_2)$  obtained in I into Eq. (1) to calculate  $\epsilon(\text{CO})$  and  $\epsilon(\text{CO}_2)$ . The calculated values so obtained were systematically lower than the average experimental  $\epsilon(\text{CO})$  and  $\epsilon(\text{CO}_2)$  by 15% and 5%, respectively, which were far outside the experimental error. The other available measurements of solid carbon thin-film stopping cross sections were those of Porat and Ramavataram.<sup>29</sup> We used the  $\epsilon(\text{O}_2)$  from I along with Porat and Ramavataram's  $\epsilon(\text{C})$  in the energy region 300–1300 keV and again found that the calculated values so obtained were still systematically lower by as much as 10.8% for  $\epsilon(\text{CO})$  and 5.7% for  $\epsilon(\text{CO}_2)$ . Thus, Bragg's rule failed to predict the observed  $\epsilon(\text{CO})$  and  $\epsilon(\text{CO}_2)$  of I by coupling  $\epsilon(\text{O}_2)$  from gaseous media with  $\epsilon(\text{C})$  from solid-target media.

A second test of Bragg's rule was made by comparing the stopping cross sections of the isomers propylene (C<sub>3</sub>H<sub>6</sub>) and cyclopropane [(CH<sub>2</sub>)<sub>3</sub>]. Table I shows the structures of these two isomers to be quite different, and one might therefore *a priori* expect the stopping to be different if the chemical bond affects the stopping process. The experimental stopping cross sections for these two substances, however, agreed to within 1%.

A third test was made by comparing the experimental stopping cross section  $\epsilon(\text{N}_2\text{O})$  to the sum  $\epsilon(\text{N}_2) + \frac{1}{2}\epsilon(\text{O}_2)$ , where  $\epsilon(\text{N}_2)$  and  $\epsilon(\text{O}_2)$  are the experimental values obtained in I. Agreement between the two was found for energies above 500 keV, but the sum  $\epsilon(\text{N}_2) + \frac{1}{2}\epsilon(\text{O}_2)$  was 5.4% higher than the experimental  $\epsilon(\text{N}_2\text{O})$  at 300 keV, thereby indicating a

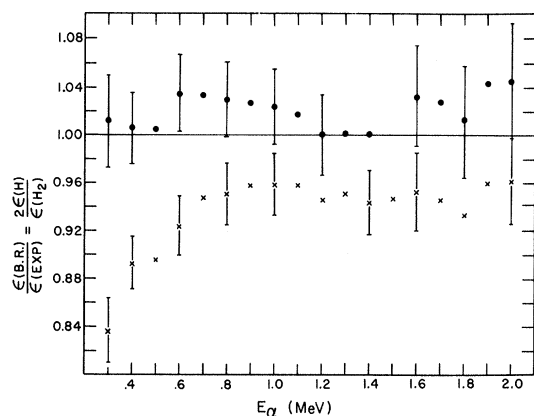


FIG. 1. Ratio of  $2\epsilon(\text{H})$ , as calculated with Bragg's rule, to  $\epsilon(\text{expt})$ , the experimentally measured stopping cross sections for  $\alpha$  particles in hydrogen.  $\times$ : calculated from hydrocarbons including  $\text{C}_2\text{H}_2$ ;  $\bullet$ : calculated from hydrocarbons excluding  $\text{C}_2\text{H}_2$ .

#### Bragg-rule deviation at low energies.

The fourth test involved hydrocarbon gases. If Bragg's rule holds,  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  can be calculated from the measured stopping cross sections of any two hydrocarbons if the two equations are algebraically independent. Twelve independent combinations of two equations exist for the experimental hydrocarbon measurements.  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  were calculated, and an average value of each was found. It should be mentioned that although the molecular stopping cross sections were measured to 2.0% or better, the  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  obtained from a given combination were only good to  $\approx 6\%$ , since the measurements are independent of one another. The average  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  so obtained were accurate from 1.9% to 2.7% and from 2.8% to 4.4%, respectively, over the entire energy region. These average values of  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  were put back into Eq. (1) to recalculate the molecular stopping cross sections and to check the reliability of the average  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$ . The stopping cross sections of  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  so calculated were less than the molecular measurements. Inspection of each individual calculated value of  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  from a given pair of equations showed that the experimental stopping cross-section measurements of  $\text{C}_2\text{H}_2$  caused systematically higher values of  $\epsilon(\text{C})$  and systematically lower values of  $\epsilon(\text{H})$  to be obtained. The deviation could have been caused by impurities in the  $\text{C}_2\text{H}_2$  gas used in the experiment, but this possibility was ruled out by the gas-chromatograph test in I.

Exclusion of the  $\text{C}_2\text{H}_2$  stopping cross-section measurement reduced the algebraically independent pairs of hydrocarbon measurements from twelve to seven. New average  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  were calculated from these seven pairs of equations. The  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  so obtained were accurate from 3.2 to 4.6%,

and from 3.6 to 6%, respectively, over the entire energy region. [The accuracy of the new average  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$  was less than that of the old average values, since fewer combinations were used in the former case to determine the averages.] These average values of  $\epsilon(\text{C})$  and  $\epsilon(\text{H})$ , when put back into Eq. (1), then gave agreement with the experimental stopping cross-section measurements for all the remaining hydrocarbons.

To make the fourth test more meaningful and to ensure that the acetylene did not obey Bragg's rule, the average hydrogen stopping cross sections calculated by the above procedure (with and without acetylene) were compared directly to the experimental stopping cross section  $\epsilon(\text{H}_2)$ . The results are given in Fig. 1, where  $2\epsilon(\text{H})$  (as calculated with Bragg's rule) is divided by the experimentally measured  $\epsilon(\text{H}_2)$  and is plotted as a ratio. A ratio of unity would indicate agreement between the Bragg-rule calculated value and the experiment. At 300 keV the Bragg-rule prediction is off by 16% and at 2 MeV by 4% when acetylene is included in the calculations.

It can then be said that molecular hydrogen obeys Bragg's rule [ $\epsilon(\text{H}_2) = 2\epsilon(\text{H})$ ], and that the hydrocarbons  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$  (propylene), and  $(\text{CH}_2)_3$  (cyclopropane) obey Bragg's rule, but acetylene does not.

The experimental  $\epsilon(\text{H}_2)$  were then used with the hydrocarbons obeying Bragg's rule to calculate a new average  $\epsilon(\text{C})$ , which was accurate from 2.0% at 300 keV to  $\approx 1.6\%$  from 400 keV to 2.0 MeV. These calculated values of  $\epsilon(\text{C})$  are given in Table II. The  $\epsilon(\text{C})$  was used with the average experimental  $\epsilon(\text{O}_2)$  to calculate  $\epsilon(\text{CO}_2)$  and  $\epsilon(\text{CO})$  by Bragg's rule as was done in the first test. The calculated values of  $\epsilon(\text{CO}_2)$  agreed with the experimental values within experimental accuracy; however, the calculated values of  $\epsilon(\text{CO})$  were lower than the experimental values by as much as 11% at 300 keV.

The results of the third and fourth tests can be interpreted in terms of the chemical structure of the molecules. Those compounds which obey Bragg's rule contain only single and double bonds. The compounds which do not obey Bragg's rule have a partial or total triple-bond character. The carbon atoms in  $\text{C}_2\text{H}_2$  are bound entirely by means of a triple bond, whereas the atoms in  $\text{CO}$  and  $\text{N}_2\text{O}$  are bound with 60% and 33 $\frac{1}{3}\%$  triple-bond character, respectively, according to Pauling.

A correction based on this triple-bond character is made in the following way. The average  $\epsilon(\text{C})$  is calculated from the hydrocarbons obeying Bragg's rule using the experimental  $\epsilon(\text{H}_2)$  as outlined above. This  $\epsilon(\text{C})$  is then used along with the experimental  $\epsilon(\text{H}_2)$  and  $\epsilon(\text{O}_2)$  to calculate  $\epsilon(\text{C}_2\text{H}_2)$  and  $\epsilon(\text{CO})$ , respectively. Figure 2 shows these calculated stop-

TABLE II. Average stopping cross section of carbon obtained from the experimental stopping cross sections of the hydrocarbons  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ , and  $(\text{CH}_2)_3$  and hydrogen using Bragg's rule. The triple-bond correction  $\Delta(\text{C}_2\text{H}_2)$  (see text for discussion) is given in column 3 along with its error in column 4.

| Energy<br>(keV) | $\epsilon(\text{C})^a$<br>( $10^{-15}$ eV cm $^2$ ) | $\Delta(\text{C}_2\text{H}_2)$<br>( $10^{-15}$ eV cm $^2$ ) | Error in $\Delta(\text{C}_2\text{H}_2)$<br>( $10^{-15}$ eV cm $^2$ ) |
|-----------------|---|---|--|
| 300             | 34.2  | 14.2  | 1.8  |
| 400             | 39.9  | 9.8   | 1.8  |
| 500             | 42.8  | 9.6   | 1.9  |
| 600             | 44.2  | 8.5   | 2.4  |
| 700             | 44.5  | 5.9   | 2.4  |
| 800             | 43.6  | 5.4   | 2.3  |
| 900             | 42.4  | 4.5   | 2.2  |
| 1000            | 40.9  | 4.2   | 2.2  |
| 1100            | 39.6  | 3.7   | 1.8  |
| 1200            | 38.2  | 3.4   | 1.8  |
| 1300            | 36.7  | 3.3   | 1.7  |
| 1400            | 35.2  | 3.8   | 1.6  |
| 1500            | 33.9  | 3.4   | 1.6  |
| 1600            | 32.7  | 3.5   | 1.7  |
| 1700            | 31.5  | 3.8   | 1.6  |
| 1800            | 30.5  | 3.6   | 1.6  |
| 1900            | 29.7  | 3.0   | 1.5  |
| 2000            | 28.8  | 2.9   | 1.5  |

<sup>a</sup>Error in  $\epsilon(\text{C})$  is 2.0% at 300 keV and 1.6% for 400 keV–2 MeV.

ping cross sections as solid triangles for  $\text{C}_2\text{H}_2$  and solid squares for CO, and the experimental points as  $\times$ 's with the average-value curve drawn through the experimental points as before. The following quantities are calculated:

$$\Delta(\text{C}_2\text{H}_2) = \epsilon(\text{C}_2\text{H}_2) - 2\epsilon(\text{C}) - \epsilon(\text{H}_2), \quad (2)$$

$$\Delta(\text{CO}) = \epsilon(\text{CO}) - \epsilon(\text{C}) - \frac{1}{2}\epsilon(\text{O}_2), \quad (3)$$

where  $\epsilon(\text{C})$  is the average calculated stopping cross section of carbon and the other stopping cross sections are the average experimental values. The values of  $\Delta(\text{C}_2\text{H}_2)$  and their estimated probable errors are also given in Table II. It is found that the ratio  $\Delta(\text{CO})/\Delta(\text{C}_2\text{H}_2)$  is roughly 60%. Since Pauling suggested a 60% triple-bond character for the binding of CO, the above ratio further suggests that a correction can be made according to whether the molecules are bound with a triple bond, or some resonance-structure fraction thereof.  $\Delta(\text{C}_2\text{H}_2)$  is taken to be the triple-bond correction; adding 60% of  $\Delta(\text{C}_2\text{H}_2)$  to the Bragg-rule prediction brings it into agreement with the experimental  $\epsilon(\text{CO})$ .

To obtain the  $\text{N}_2\text{O}$  correction, one first notices from Table I that  $\text{N}_2$  has a 100% triple-bond structure, so that  $\epsilon(\text{N}_2) = 2\epsilon(\text{N}) + \Delta(\text{C}_2\text{H}_2)$ . Since, according to Pauling, the structure of  $\text{N}_2\text{O}$  is one-third triple bond, and since we are neglecting the influence of the double bond on the stopping process, the

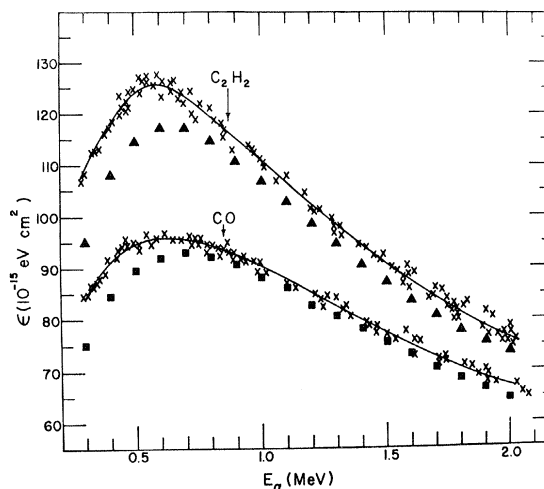


FIG. 2. Comparison of experimental and Bragg-rule predictions of  $\epsilon(\text{C}_2\text{H}_2)$  and  $\epsilon(\text{CO})$ .  $\times$ 's are the experimental stopping cross sections of  $\text{C}_2\text{H}_2$  and CO using the differentially pumped gas cell in I. Each curve is an average-value curve drawn through the experimental measurements.  $\blacktriangle$  are  $2\epsilon(\text{C}) + \epsilon(\text{H}_2)$  (see text) and  $\blacksquare$  are  $\epsilon(\text{C}) + \frac{1}{2}\epsilon(\text{O}_2)$  (see text).

stopping cross section for  $\text{N}_2\text{O}$  would be

$$\begin{aligned} \epsilon(\text{N}_2\text{O}) &= 2\epsilon(\text{N}) + \frac{1}{2}\epsilon(\text{O}_2) + \frac{1}{3}\Delta(\text{C}_2\text{H}_2) \\ &= \epsilon(\text{N}_2) + \frac{1}{2}\epsilon(\text{O}_2) - \frac{2}{3}\Delta(\text{C}_2\text{H}_2). \end{aligned}$$

This correction brings the Bragg-rule prediction with triple-bond correction into complete agreement with the experimental  $\epsilon(\text{N}_2\text{O})$  over the entire energy region.

The fifth test of Bragg's rule involved  $\epsilon(\text{N}_2)$ ,  $\epsilon(\text{H}_2)$ , and  $\epsilon(\text{NH}_3)$ . As mentioned above,  $\text{N}_2$  has a 100% triple-bond structure, whereas according to Table I, the atoms of  $\text{NH}_3$  are connected only with single bonds which should produce negligible effects

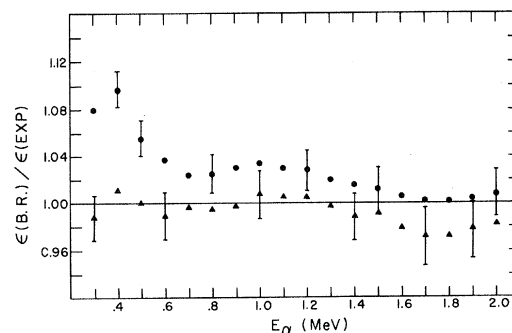


FIG. 3. Ratio of  $\frac{1}{2}\epsilon(\text{N}_2) + \frac{3}{2}\epsilon(\text{H}_2)$  to  $\epsilon(\text{expt})$ , the experimentally measured stopping cross sections for  $\alpha$  particles in ammonia  $\text{NH}_3$ , and the ratio of  $\frac{1}{2}[\epsilon(\text{N}_2) - \Delta(\text{C}_2\text{H}_2)] + \frac{3}{2}\epsilon(\text{H}_2)$  to  $\epsilon(\text{expt})$  (see text for discussion).  $\bullet$ :  $[\frac{1}{2}\epsilon(\text{N}_2) + \frac{3}{2}\epsilon(\text{H}_2)]/\epsilon(\text{expt})$  and  $\blacktriangle$ :  $\{\frac{1}{2}[\epsilon(\text{N}_2) - \Delta(\text{C}_2\text{H}_2)] + \frac{3}{2}\epsilon(\text{H}_2)\}/\epsilon(\text{expt})$ .

on the stopping process according to the first four tests. Figure 3 shows the ratio of the Bragg-rule prediction  $\frac{1}{2}\epsilon(\text{N}_2) + \frac{3}{2}\epsilon(\text{H}_2)$  with no triple-bond correction to the experimentally measured  $\epsilon(\text{NH}_3)$ . The ratio of the Bragg-rule prediction with triple-bond correction  $\frac{1}{2}[\epsilon(\text{N}_2) - \Delta(\text{C}_2\text{H}_2)] + \frac{3}{2}\epsilon(\text{H}_2)$  to  $\epsilon(\text{NH}_3)$  is also plotted in the figure. It is seen that without triple-bond correction, the data disagree by as much as 9.6% at 400 keV, but the Bragg-rule prediction with triple-bond correction fits the measured  $\epsilon(\text{NH}_3)$  to within experimental accuracy.

The following rather surprising conclusions can be drawn from the stopping of  $\alpha$  particles in various gaseous compounds in the energy region 0.3–2.0 MeV: (a) Bragg's rule holds for compounds containing single and double bonds. (b) Compounds containing triple bonds deviate from Bragg's rule, but an empirical triple-bond correction can be made to fit all the experimental data. (c) The fact that the empirical correction to fit the CO measurements is 60% of the  $\text{C}_2\text{H}_2$  correction supports in part the resonance structure of CO due to Pauling involving a triple-bond character. (d) The fact that the empirical correction to fit the  $\text{N}_2\text{O}$  measurements is two-thirds of the  $\text{C}_2\text{H}_2$  correction supports in part the resonance structure due to Pauling involving in  $\text{N}_2\text{O}$  a one-third contribution from the structure containing a nitrogen-nitrogen triple bond.

### III. COMPARISON WITH OTHER EXPERIMENTAL DATA

Reynolds *et al.*<sup>15</sup> measured the stopping cross sections of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ , and of several hydrocarbon gases including  $\text{C}_2\text{H}_2$  for protons in the energy region 30–600 keV. We have treated their proton data in the same manner as the  $\alpha$ -particle data in the present analysis. It was found that  $\text{CO}_2$  obeyed Bragg's rule for protons as well as  $\alpha$  particles. The triple-bond corrections necessary

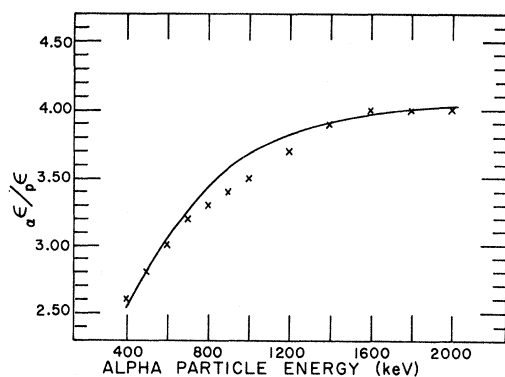


FIG. 4. Ratio  $\alpha\epsilon/p\epsilon$  of the stopping cross sections for  $\alpha$  particles (present experiment) to that for protons (Ref. 15) of the same velocity is given by the smooth curve. The  $\times$ 's are given by Whaling ( $\pm 20\%$ ) (Ref. 31).

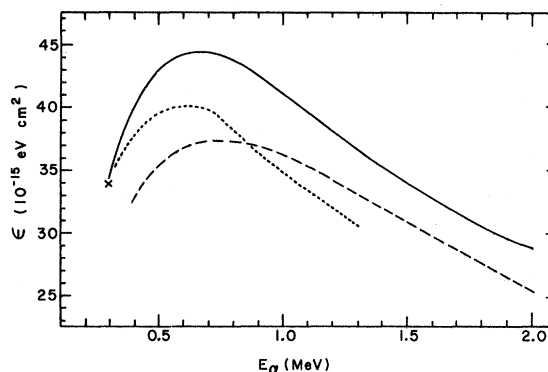


FIG. 5. Stopping cross sections of  $\alpha$  particles in carbon. Smooth curve is the average calculated value from the hydrocarbon gases excluding  $\text{C}_2\text{H}_2$ . Dashed curve represents the measurements by Chu and Powers (Ref. 28) in solid C, the  $\times$  is by Sautter and Zimmerman (Ref. 32) in solid C, and the dotted curve gives the measurements by Porat and Ramavaram (Ref. 29) in solid C.

to fit the  $\alpha$ -particle stopping cross sections were also necessary to fit the proton stopping cross sections of  $\text{NH}_3$  and of  $\text{N}_2\text{O}$ . Reynolds *et al.* also found a deviation from Bragg's rule for both  $\text{NO}$  and  $\text{H}_2\text{O}$ . They suggested the possibility of contamination of the  $\text{NO}$  gas as the cause of the deviation for  $\text{NO}$ , since  $\text{NO}$  readily oxidizes to  $\text{NO}_2$  in the presence of air. A triple-bond correction to their  $\text{N}_2$  data does not cause the deviation for  $\text{NO}$  to vanish.  $\text{H}_2\text{O}$  would also be expected to obey Bragg's rule, since its structure contains only single bonds. However, such agreement was not observed by Reynolds, and the reason for this deviation is not known. Nevertheless, the Bragg rule with empirical triple-bond correction fits the present data and all their data except for  $\text{NO}$  and  $\text{H}_2\text{O}$ .

It is of interest in comparing Reynolds's data to the present data that the ratio  $\alpha\epsilon/p\epsilon$  of the stopping cross sections for  $\alpha$  particles to that for protons of the same velocity is independent of the stopping material to better than 4% for  $E_\alpha > 1000$  keV and is no worse than 6.5% for  $400 \text{ keV} < E_\alpha < 800$  keV. This ratio varies from 2.54 for 400-keV  $\alpha$  particles to 4.03 for 2000-keV  $\alpha$  particles, and is plotted as a function of energy in Fig. 4. Andersen *et al.*<sup>30</sup> also found the ratio to be greater than 4.00 for proton energies above 2.5 MeV in Ta and Al.

The conclusions reached in Sec. II B are based on the agreement of the experimental hydrogen stopping cross sections with the average calculated hydrogen stopping cross sections (from the hydrocarbons excluding  $\text{C}_2\text{H}_2$ ) being used as the criterion for the validity of Bragg's rule. However, another criterion would be the agreement of the experimental stopping cross sections with the average calculated atomic carbon stopping cross sections (from

the hydrocarbons excluding  $C_2H_2$ ). Figure 5 shows the average calculated carbon stopping cross sections (from the hydrocarbons excluding  $C_2H_2$ ) and the experimentally measured stopping cross sections of carbon by Chu and Powers<sup>28</sup> of this laboratory. The calculated values from gaseous media are greater than the measured values in solids by 22.4% at 400 keV to 13% at 2 MeV. Sautter and Zimmerman<sup>32</sup> have found a similar behavior for protons in hydrocarbons. Their calculated carbon stopping cross sections from gases for protons are greater than the measured values in solids by 26% at 50 keV and 13% at 300 keV. They also show that the stopping cross section in gases are always higher than solids by as much as 15%. The measurement by Sautter and Zimmerman in solid carbon at 300 keV is also shown in Fig. 4 along with the measurements from 300 to 1300 keV by Porat and Ramavataram.<sup>29</sup> The reason for the disagreement of the measurements in solid carbon by different experimental groups is not known. Booth and Grant<sup>33</sup> find a discrepancy between their  $dE/dx$  measurements of oxygen ions in carbon films. The tests that were run on the carbon films for adsorption in I, however, indicate that the original measurements of Chu and Powers could be off by no more than 3.8% from the adsorption of impurities onto the carbon films. Those tests give strong support to the validity of the measurements by Chu and Powers and verify the meaningfulness of using those measurements in the present discussion. It therefore seems reasonable to conclude that atomic stopping cross sections calculated from gaseous molecular data should not be applied rigorously to stopping by the same atomic substance in the solid state.

#### IV. CONCLUSION

The applicability of Bragg's rule to the data of the present experiment I can be stated as follows: (a) Bragg's rule applies to the gaseous compounds which contain single and double bonds. (b) Bragg's rule does not apply to compounds containing triple bonds, but an empirical correction can be made to fit the data of these compounds.

The calculated average  $\epsilon(C)$  does not agree with the  $\epsilon(C)$  of solid carbon measured by Chu and Powers of this laboratory. This deviation suggests a possible physical-state effect. The solid-carbon measurements by different experimental groups, however, deviate from one another by almost as much as the solid and gas measurements do. Further investigation regarding the physical-state effect is needed and is contemplated in this laboratory. In light of the evidence reported here, however, it is questionable whether the present  $\epsilon(C)$  for  $\alpha$  particles or the  $\epsilon(C)$  for protons by Reynolds *et al.* obtained from gaseous compounds apply to calculations involving C in the solid state.

It is also doubtful that one-half the molecular stopping cross section of nitrogen is equal to the atomic stopping cross section of nitrogen for protons or  $\alpha$  particles. Also, based on the present analysis, the atomic stopping cross sections of hydrogen and oxygen are given by one-half their respective molecular stopping cross sections.

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PHYSICAL REVIEW B

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## Vectorial Photoelectric Effect

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Experimental results and their analysis are presented which indicate that the vectorial photoelectric effect originates neither in excitation at the surface nor in pure volume optical absorption, but is a unique combined surface-volume effect which depends only on optical absorption as influenced by the interface. This effect can be phenomenologically regarded as surface-enhanced optical absorption (SEOA) in which, for certain transitions excited by light polarized perpendicular to the surface, optical absorption in the volume near the surface can be increased manifoldly (100 times or more) by the presence of certain surface conditions. Our results show a large decrease in this absorption by controlled modification of the surface for the system investigated, which is single-crystal silicon in ultrahigh vacuum with surfaces oriented parallel to (111), (110), and (100) planes. Photoelectric yields are shown at angles of incidence from 0° to 60° for both polarized and unpolarized light with photon energies in the range 4.6–6.4 eV. Some interface effects are illustrated by photoemission from samples covered with thin (20–100 Å) oxide layers; electron emission is considered in terms of the system silicon-silicon oxide-vacuum. Essential requirements are discussed for a theory of SEOA, the existence of which calls for a reexamination of present approaches to the fundamental theory of photoelectric emission.

### I. INTRODUCTION

Photoelectric emission includes several processes: optical absorption by excitation of electrons, motion of the excited carriers, and emission into the collecting medium through the interface. The determination of the spatial and temporal location of these processes, from the earliest days, has been central to the analysis of photoelectric emission, which requires, whatever the mechanism, that conservation of momentum be provided for in the photon-electron interaction.

For many years it was believed, for metals at least, that all processes occurred simultaneously at (within a few angstroms of) the surface. Conservation of momentum in theories<sup>1-4</sup> taking this viewpoint (the "surface photoeffect") is provided at the potential step between the surface and collecting medium (usually vacuum). In such theories, only the component of polarization of the light parallel to the gradient of the potential step, and thus perpendicular to the surface, will cause photoexcitation. And indeed, earlier experimental results<sup>5,6</sup> seemed to be consistent with the qualitative predictions of these theories in that photoelectric measurements showed greater yields for radiation with polariza-

tion components perpendicular to the surface. This result was called the "vectorial photoelectric effect" by Ives<sup>6</sup> for reasons which, it is now realized, are not applicable; however, we shall continue with the same terminology, since it has become established by usage. In fact, the difficulties in comparing experiment with theory were not in observing the vectorial effect, but rather in explaining the appreciable yields measured with illumination at normal incidence (necessarily with polarization parallel to the plane of the surface). Normal-incidence yields were generally explained by the introduction of the obvious mechanism of surface roughness.<sup>1</sup> However, the required amount of surface roughness has seemed arbitrary, and there has been no direct correlation available between experiment and theory.

The opposing concept, that optical absorption occurs simply within the volume of the material, was introduced and theoretically developed in 1945 by Fan,<sup>7</sup> who pointed out that momentum would be conserved in volume absorption because electrons move in a periodic potential. Subsequently, the resolution of the surface-volume question was apparently obtained by Thomas and co-workers who, in a series of papers<sup>8-10</sup> on photoelectric emission from thin