

Electronic Stopping in a He-H₂ Mixture Substantially Exceeds Bragg's Rule Value

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We measured the energy loss of 8-keV deuterons in mixtures of He and H₂ gases using a time-of-flight technique. According to Bragg's rule the stopping cross section ε of a mixture of nonreacting gases should be the weighted average of the stopping cross sections of its constituents. Experimentally we find ε to exceed the Bragg value by more than 50%. This can be traced to large differences in the electron capture and electron loss cross sections of He and H₂, respectively, that strongly enhance energy losses due to charge-changing collisions.

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The mean energy loss of swift ions in matter—the electronic stopping cross section ε —is a key quantity for many ion beam applications, e.g., for ion implantation, for ion beam modification of materials, for particle identification, for medical and health physics dosimetry, etc. The projectile energy range of interest is extremely broad, say, 10 eV to 1 GeV, and, even if one thinks of single-element targets only, the number of projectile-target combinations is of the order of 10^4 . In many cases, ε need to be known with an accuracy of a few percent; in most cases errors larger than 10% are unacceptable. The Bethe-Bloch theory describes only light projectile ions at large energies E_1 . Around the stopping power maximum and below, semiempirical data have to be used, e.g., by Ziegler, Biersack, and Littmark [1]. Low velocity hydrogen projectiles play a key role, since one can extrapolate from proton stopping to heavy ion stopping at the same projectile velocity by the so-called effective charge concept [1].

For the stopping cross section of multielement targets, either compounds or mixtures, Bragg's rule of linear additivity [2] is commonly applied. At projectile velocities well above the stopping power maximum, the accuracy of Bragg's rule is comparable to the accuracies of the single-element values. At the stopping power maximum and below, the values from Bragg's rule for *compounds* may deviate from measured values by some 10% [3]. Up to now, no deviation has been measured for mixtures, and Bragg's rule is supposed to be strictly valid. In this paper we show experimentally that linear additivity can be quite wrong even for a mixture of nonreacting gases. The energy loss of 8-keV deuterons in a He-H₂ mixture is more than 50% larger than the value calculated by Bragg's rule. This enormous deviation, compared to the aimed degree of accuracy, can be explained by an indirect interaction of the target components via the projectile charge state. We have predicted this effect in Ref. [4], and we will briefly summarize our model below. The measured effect highlights the importance of charge-changing collisions for

electronic stopping and shows that projectiles do not lose energy only in a passive way but play an active role in the stopping process. Although we do not expect the effect to be equally large for mixtures of other gases, it may well outweigh the errors of the single-element values. We wish to point out that the energy loss in tissue equivalent gas mixtures is of particular importance in medical and health physics dosimetry. Possible implications for solid targets are given in the conclusion.

Bragg's rule [2] of linear additivity states that the electronic stopping cross section ε^{AB} of a two-component target AB is the weighted mean of the stopping cross sections ε^A and ε^B of its constituents A and B ,

$$\varepsilon^{AB} = c_A \varepsilon^A + c_B \varepsilon^B, \quad (1)$$

where c_A and $c_B = 1 - c_A$ are the molar fractions of components A and B , respectively. The electronic stopping cross section is defined by

$$\varepsilon = \sum_i T_i \sigma_i(E_1). \quad (2)$$

T_i denotes the energy transfer from the projectile to the target for a collision process i , and σ_i is the corresponding cross section at projectile energy E_1 ; the sum extends over all momentum transfers and all final states. Obviously, linear additivity can fail when A and B form a *compound*. Because of chemical binding, some of the values of T_i and σ_i can change, leading to well-known deviations from Bragg's rule for compounds [3].

In Ref. [4] we suggested a simple model by which the failure of linear additivity for a He-H₂ mixture can be estimated. Briefly, the argument runs as follows. At 4 keV per nucleon, hydrogen projectiles in He or in H₂ are either protons (charge state 1) or neutral atoms (charge state 0); negatively charged ions can be neglected. In dynamic equilibrium, the corresponding charge-state populations are $F_1 = \sigma_{0 \rightarrow 1} / (\sigma_{1 \rightarrow 0} + \sigma_{0 \rightarrow 1})$ and $F_0 = \sigma_{1 \rightarrow 0} / (\sigma_{1 \rightarrow 0} + \sigma_{0 \rightarrow 1}) = 1 - F_1$, respectively. Here $\sigma_{0 \rightarrow 1}$ denotes the stripping cross section

(ionization of the projectile by the target) and $\sigma_{1\rightarrow 0}$ is the cross section for electron capture, where both $\sigma_{0\rightarrow 1}$ and $\sigma_{0\rightarrow 1}$ have to be understood as averaged over all possible initial and final states. We rewrite Eq. (2) in such a way that collision processes with frozen projectile charge state and charge-changing collisions are shown explicitly:

$$\varepsilon = F_1 \sum_i T_i \sigma_{i,1} + F_1 \bar{U} \sigma_{1\rightarrow 0} + F_0 \sum_i T_i \sigma_{i,0} + F_0 \bar{K} \sigma_{0\rightarrow 1}. \quad (3)$$

In Eq. (3) we distinguish between collision processes of bare protons (first term) and of neutral hydrogen atoms (third term) that lead to an energy transfer T_i with cross sections $\sigma_{i,1}$ and $\sigma_{i,0}$, respectively, but that do not change the projectile charge state. The second and the fourth terms describe charge-changing collisions: When a proton captures a target electron, the mean ionization energy \bar{U} of the target is transferred on the average, and in the stripping process the target gains on the average the mean kinetic energy \bar{K} of the released electron. (This simple picture only provides a qualitative insight into the role of charge-changing processes. A comprehensive scheme with a high degree of rigor has been presented recently by Sigmund [5].)

When we proceed from the pure gases to the He-H₂ mixture with molar fractions $c_{\text{He}}, c_{\text{H}_2}$, respectively, all terms in Eq. (3) have to be replaced by the weighted contributions of both constituents (as suggested by Bragg's rule). The charge-changing cross sections add linearly:

$$\sigma_{0\rightarrow 1}^{\text{He,H}_2} = c_{\text{H}_2} \sigma_{0\rightarrow 1}^{\text{H}_2} + (1 - c_{\text{H}_2}) \sigma_{0\rightarrow 1}^{\text{He}}, \quad (4a)$$

$$\sigma_{1\rightarrow 0}^{\text{He,H}_2} = c_{\text{H}_2} \sigma_{1\rightarrow 0}^{\text{H}_2} + (1 - c_{\text{H}_2}) \sigma_{1\rightarrow 0}^{\text{He}}. \quad (4b)$$

However, the charge-state populations $F_0^{\text{He,H}_2} = \sigma_{1\rightarrow 0}^{\text{He,H}_2} / (\sigma_{1\rightarrow 0}^{\text{He,H}_2} + \sigma_{0\rightarrow 1}^{\text{He,H}_2}) = 1 - F_1^{\text{He,H}_2}$ behave in a nonlinear way, and this leads to a deviation of $\varepsilon^{\text{He,H}_2}$ from Bragg's rule. Obviously, at high energies, where $F_0 \approx 0$ for all target materials, Bragg's rule is valid. To calculate the charge-state populations at low energies, e.g., for 4-keV hydrogen projectiles, we use the charge-changing cross sections $\sigma_{0\rightarrow 1}^{\text{He}} = 1.1$, $\sigma_{1\rightarrow 0}^{\text{He}} = 0.20$, $\sigma_{0\rightarrow 1}^{\text{H}_2} = 0.43$, and $\sigma_{1\rightarrow 0}^{\text{H}_2} = 4.7$, in units of 10^{-16} cm^2 [6]. We note that helium has a dominant stripping cross section, whereas hydrogen has a dominant capture cross section. For the pure gases, stopping is comparatively small due to a certain compensation: In helium $F_1 \approx 0.85$ is large, but $\sigma_{1\rightarrow 0}$ is small; in hydrogen $F_1 \approx 0.08$ is small, so the large value of $\sigma_{1\rightarrow 0}$ has little effect.

Such a compensation does not occur for the mixture. Adding a small amount of hydrogen to helium increases $\sigma_{1\rightarrow 0}^{\text{He,H}_2}$ and, hence, the neutral charge-state population; e.g., for $c_{\text{H}_2} = 0.2$, $F_0^{\text{He,H}_2} = 0.53$ at 4 keV, whereas linear interpolation would only give 0.30. With a large $F_0^{\text{He,H}_2}$, the large stripping cross section of He becomes very effective. Thus, adding H₂ to He speeds up the

charge-changing cycle and greatly increases the stopping cross section beyond the Bragg value.

The experimental layout is basically similar to that described in [7,8]. Here we give only a short description of our time-of-flight (TOF) method and of the preparation of the He-H₂ mixtures. We used 8-keV deuterons as projectiles, which suffer essentially the same energy loss as 4-keV protons. Ten different target compositions including the pure gases He and H₂ have been investigated with target pressures between 0.01 and 0.05 mbar. A differentially pumped aperture (0.25 cm in diameter) forms the beam entrance into the target chamber (210 cm in length), and a carbon foil of 150 Å thickness covers the target exit hole of 0.4 cm in diameter. The energy loss was derived from the difference in TOF when the chopped beam traverses the target chamber with and without gas, respectively [9]. The start of the TOF measurement is triggered by the chopper electronics; the stop signal is derived from a microchannel plate mounted 3.1 cm downstream of the exit foil. Our time resolution is of the order of 1 ns. Because of multiple scattering in the target gas the probability that two or more particles per pulse reach the stop detector is less than 10^{-4} . The chopper typically runs at 100 kHz; the count rate with 0.01 mbar is about 1.2×10^3 counts per second.

In principle our transmission geometry could simulate an apparent deviation from Bragg's rule due to large-angle scattering [10]. This is a consequence of impact parameter selection [8]: Projectiles which have probed the inner regions of atoms and hence have lost a comparatively large amount of energy may be scattered out of the detector acceptance. Increasing the target density reduces this effect as projectiles may now be rescattered into the detector with higher probability. Thus an apparent pressure dependence of ε will be measured. For a He-Ne mixture the possible error is of the order of 5%, but for a He-H₂ mixture, it must be very small. We checked both by experiment and by Monte Carlo simulation that the systematic error due to impact parameter selection for hydrogen projectiles in H₂ or in He is less than 1%.

To calculate ε from the measured energy losses, we have to know c_{H_2} and $c_{\text{He}} = 1 - c_{\text{H}_2}$. For a direct measurement by a quadrupole mass spectrometer (QMS), the target pressures were too high. However, even at sufficiently low pressure, hydrogen gas leads to well known difficulties. We have therefore used the QMS only for qualitative measurements and have followed two different approaches to determine $c_{\text{H}_2}, c_{\text{He}}$ quantitatively: (I) by preparing well defined mixtures at a relatively high pressure (10^2 mbar) outside the target chamber, and (II) by introducing well controlled flows of the pure gases into the chamber from two separate bottles.

The advantage of method I is that we can easily determine the external concentrations with an accuracy better than 1% since they only depend on ratios of volumes and pressures. This method might suffer from

gas fractionation at the input valve [11], where gas flow changes from hydrodynamic to molecular. Indeed, we have observed fractionation with Ar-He mixtures at the percent level, but we did not observe it with He-H₂ mixtures. However, there will certainly be fractionation due to molecular flow into the differential pumping stage. We found that this fractionation is independent of pressure up to 0.05 mbar and depends only on the square root of the molecular mass ratio, and therefore we were able to correct the external concentrations appropriately.

Method II relies on the fact that the mass flows of He and H₂ through the respective input valves of the two bottles are fairly constant in time. For setting up a certain mixture in the target chamber, the equilibrium partial pressure was first established for one component and then the second component was admitted to give the required total pressure. After several energy loss measurements with the mixture, the mass flow of the first component remained constant. The advantage of method II is that there can be no fractionation at the input stage, and fractionation due to gas flow into the differential pumping stage is of no concern either, since the partial pressures were measured directly. Finally, we compared the stopping cross sections obtained by the two methods; the results agree within a few percent. We estimate the maximum absolute uncertainty of c_{H_2} and $c_{\text{He}} = 1 - c_{\text{H}_2}$ to be about 2%. The absolute error of our stopping cross section measurement is $\pm 0.1 \times 10^{-15} \text{ eV cm}^2$. It comes mainly from the capacitive pressure gauge, from the drift of beam energy, from changes of the time shift by the exit foil under gas load, and from uncertainties of the first moment of the time-to-energy converted spectra [9]; a detailed analysis is given in [7].

In Fig. 1 the measured stopping cross sections of several He-H₂ mixtures for 8-keV deuterons are plotted as a function of the atomic fraction of hydrogen, $c_{\text{H}} = 2c_{\text{H}_2}/(1 + c_{\text{H}_2})$; the values for pure He and for pure H₂ at different target pressures are plotted at $c_{\text{H}} = 0$ and $c_{\text{H}} = 1$, respectively; an error bar is shown at $c_{\text{H}} = 0.4$. The dashed line is the prediction according to Bragg's rule of linear additivity, the dotted line marks a 50% increase beyond Bragg's rule, and the shaded area is our prediction [4].

For pure helium, we find a mean value $\varepsilon^{\text{He}} = 0.80 \times 10^{-15} \text{ eV cm}^2$. This agrees well with our earlier value $0.72 \times 10^{-15} \text{ eV cm}^2$ [7]. For pure hydrogen, we find $\varepsilon^{\text{H}_2} = 2.59 \times 10^{-15} \text{ eV cm}^2$; the previous value was $2.69 \times 10^{-15} \text{ eV cm}^2$ [12]. The measured data points $\varepsilon^{\text{He,H}_2}$ for the mixtures are substantially beyond the Bragg rule values (for $0.2 \leq c_{\text{H}} \leq 0.4$ the deviation is greater than 50%), but $\varepsilon^{\text{He,H}_2}$ is well within the region predicted in Ref. [4].

The surprisingly good agreement between the measured data and the predicted values can be explained by the extraordinary simplicity of our collision system. Only here the two-state approach is sufficiently well justified

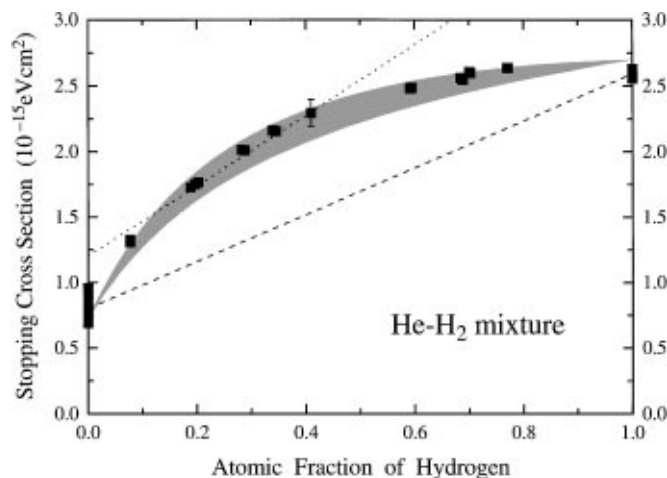


FIG. 1. Stopping cross section of a He-H₂ mixture for deuterons at 4 keV per nucleon as a function of the atomic fraction of hydrogen gas c_{H} . (■) measured values; dashed line, prediction from Bragg's rule; and dotted line, 50% increase beyond Bragg's rule. The shaded area is our prediction [4] based upon the charge-changing cross section from Ref. [6].

and the relevant cross sections are well known. For heavier projectiles (e.g., He projectiles) or heavier targets, excited states and multielectron transitions make the two-state approach inappropriate. Even if the relevant cross sections are available, their errors do not allow one to predict whether or not a similar effect might arise.

There is evidence that in insulators the dependence of ε on v_1 reflects the partition of energy losses into frozen-charge processes and charge-changing processes. Mixtures of gases like He and H₂ provide an ideal method to only modify the contribution of charge-changing events and to investigate its effect upon the velocity dependence. Charge-changing collisions also contribute to stopping in solid targets [13]. We are convinced that comparing the dependence of ε on v_1 in gas mixtures to the velocity dependence in solids can contribute to the long standing questions: What is the projectile charge state within a solid insulator? And what is the magnitude of charge-changing collisions in those materials?

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