Electronic stopping in oxides beyond Bragg additivity

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Abstract
We present stopping cross sections calculated by our PASS code for several ions in metal oxides and SiO\textsubscript{2} over a wide energy range. Input takes into account changes in the valence structure by assigning two additional electrons to the 2p shell of oxygen and removing the appropriate number of electrons from the outer shells of the metal atom. Results are compared with tabulated experimental values and with two versions of Bragg's additivity rule. Calculated stopping cross sections are applied in testing a recently-proposed scaling rule, which relates the stopping cross section to the number of oxygen atoms per molecule.

Keywords: Stopping power, compounds, Bragg additivity, PASS code, light ions, heavy ions.

1. Introduction

This note addresses the stopping of charged particles in media containing more than one atomic species, as exemplified by metal and semiconductor oxides. A convenient standard of reference is the so-called Bragg additivity rule which assumes that the stopping cross section of an aggregate equals the sum of the stopping cross sections of the constituent atoms. This model ignores differences in electronic structure between an isolated atom and an atom bound in an aggregate. The error made by adopting Bragg additivity depends on ion species and energy and, of course, on the physical state and chemical composition of the material.

Stopping cross sections of atoms have been measured for numerous ion-target combinations over a wide range of energies, and theoretical schemes have been developed that produce numbers comparable in accuracy with measured ones [1,
In principle, such theoretical schemes can also be applied to molecules and aggregates. But with few exceptions, stopping parameters of compounds are still determined from Bragg’s rule.

While we do find it tempting to use experimental or theoretical stopping data for elemental materials for estimating stopping parameters in compound media, we wish to replace Bragg additivity by a more accurate scheme, yet with a similarly appealing degree of simplicity.

Our approach has been stimulated by a recent paper by Roth et al. [3], who measured stopping cross sections of oxides for protons with \( v < v_0 \), where \( v_0 \) is the Bohr speed. They concluded that the stopping cross section of an oxide is essentially determined by the number of oxygen atoms. This is not unexpected, since stopping at low velocities is mainly due to outer-shell electrons, i.e., primarily by two valence electrons per oxygen atom.

We explore this picture on the basis of our PASS code, which has been probed on a large number of ions and target atoms [4, 2]. This code, based on binary stopping theory [5], computes stopping parameters separately for individual target and projectile shells. Electron configurations are characterized by shell binding and mean excitation energies as well as orbital speeds. Changes from free to bound atom configurations can be accomplished by switching occupation numbers.

We compare stopping cross sections calculated by PASS on the basis of Bragg’s rule as well as two modified versions and compare with most available experimental data. Thereafter we try to explore scaling properties. As it turns out, a slightly modified version of the scaling rule proposed by Roth et al. [3] is fulfilled with surprising accuracy.

2. **The model**

Binary stopping theory [5] is an extension of Bohr stopping theory [7] which has been implemented in the PASS code [4]. In its present form this code incorporates shell and Barkas-Andersen corrections, projectile screening and excitation, charge exchange in equilibrium, an inverse-Bloch correction to account for the transition to the Bethe regime, and relativistic effects [2]. Stopping cross sections from PASS have been compared extensively with measurements on elemental targets, initially [4, 2] for ions with atomic numbers \( 3 \leq Z_1 \leq 18 \), but subsequently also for antiprotons [8], heavier ions [9] and, most recently, for protons [10].

Input parameters entering the pass code are binding energies \( U_{n\ell} \) and \( I \)-values (mean excitation energies) \( I_{n\ell} \) as well as orbital velocity spectra of projectile and target atom. For metals the valence shell is treated as a free electron gas.
Figure 1: Stopping cross sections per molecule for protons on oxides. Experimental data compiled and referred to in ref. [6] and [3]. Lines found from PASS for three options (I)-(III) defined in the text.
We apply shell binding energies \( U_{n\ell} \) from ref. [11]. \( I_{n\ell} \) for selected elements have been tabulated in ref. [2]. With the exception of oxygen we apply \( I_{n\ell} \)-values related to \( U_{n\ell} \) via the SBS scheme [12] in the present context. With this we obtain a unique set of binding energies also for outer subshells.

In the following we explore three options for evaluating stopping cross sections for oxides:

(I) Straight Bragg: The stopping cross section per molecule\(^1\) is equal to the sum of stopping cross sections of the constituents.

(II) Modified Bragg: This option differs from (I) in the treatment of the valence shell of the metal atom, which is treated as a free electron gas in (I). Since oxides are insulators, we instead treat the valence shell as that of an isolated atom.

(III) Compound: We assign 2 additional electrons to the 2p shell of oxygen and subtract the appropriate number, e.g., 5 for Ta\(_2\)O\(_5\), from the metal subshell(s). Neither \( U_{n\ell} \) nor \( I_{n\ell} \) are changed.

3. Stopping Cross Sections

Figure 1 shows stopping cross sections for H ions on a number of oxide materials for which experimental data exist. Included are theoretical curves based

\(^1\)We denote the basic unit of a compound a molecule, even though the target is most often not a molecular gas
on options (I)-(III) defined above. For SiO$_2$ there are only two curves, since the valence shell in elemental Si is not described as a free electron gas.

We find a significant difference, up to a factor of two, between the straight-Bragg and compound options, while the modified-Bragg option yields intermediate results. The difference is most pronounced at low to intermediate beam energies, but it does not vanish at high speed. This must be so, since the total $I$-value changes with a change in occupation numbers of subshells.

The agreement between calculations and experiment varies significantly from system to system. As could be expected, agreement is good in the Bethe regime, i.e., well above the stopping maximum. In the region around the maximum, PASS predictions tend to lie below experimental values already for elemental targets [4]. This has the effect that the straight Bragg option actually delivers data close to experimental values in that energy range.

At low speed, conventionally called the velocity-proportional regime, deviations lie in the 10-20% range for VO$_2$, HfO$_2$ and Ta$_2$O$_5$. For Al$_2$O$_3$ – which is the system best covered with experimental data – the scatter is exceptionally large, but the agreement between our ‘compound’ curve and the most recent data [3] is close to perfect within experimental scatter.

An attempt to match these data to a power law will in all cases lead to exponents greater than 0.5. This feature is wellknown for elemental targets [13]. We have shown recently [10] that in stopping measurements in transmission geometry, a restricted stopping cross section is measured which deviates from the total stopping cross section. The difference depends on detector geometry and beam energy and may become substantial, greater than a factor of 2 at energies near the lower limit of the scale. We have asserted that impact-parameter dependence also affects measurements in reflection geometry, but an attempt to estimate the magnitude of this effect is still on the way.

We may conclude that for proton beams, adopting Bragg additivity overestimates the stopping cross sections by up to a factor of 2 in the velocity range below the maximum. This was already observed by Roth et al. [3] on the basis of experimental stopping data.

Figure 2 shows corresponding graphs for Helium ions in SiO$_2$ and HfO$_2$. Similar results (not shown) have been found for Al$_2$O$_3$, TiO$_2$ and ZnO. Experimental data found in ref. [6] cover mostly the energy range around the stopping maximum. An exception is SiO$_2$, where we find near-perfect agreement with the curve labeled ‘compound’ in the velocity-proportional regime.

Figure 3 shows similar comparisons for C, N, O and Cl ions in Al$_2$O$_3$, SiO$_2$ and Ta$_2$O$_5$.

Considerable scatter is seen between measurements from different
Figure 3: Same as Figure 1 for C, N, O and Cl ions in Al₂O₃, SiO₂ and Ta₂O₅. Experimental data compiled and referred to in ref. [6].
Figure 4: Contributions from individual subshells to stopping cross section of H in Al$_2$O$_3$ and HfO$_2$. Total T and Total TP denote the total stopping cross section per molecule excluding and including projectile excitation, respectively.

sources. For Al$_2$O$_3$ and Ta$_2$O$_5$ the lowest data sets come close to the curves labeled ‘compound’. For SiO$_2$ experimental data come closer to the Bragg curves. We note that the difference between Bragg and compound decreases with increasing atomic number $Z_1$ of the ion, a conclusion we arrived at long ago [14].

4. Contributions from Individual Shells

Figure 4 shows contributions to the stopping cross section of H in Al$_2$O$_3$ and HfO$_2$ from individual subshells. In the low-energy range the 2p subshell of oxygen, to which have been assigned 2 additional electrons in our model, dominates both cases. Also 2s electrons of oxygen contribute significantly. At low energies a noticeable contribution also stems from projectile excitation. In Al$_2$O$_3$ the contribution of the Al-2p shell lies an order of magnitude below that of the O-2p shell. In case of HfO$_2$ the contribution of the Hf-5p shell lies close to that of O-2s.

At the high-energy end, contributions to the stopping cross sections are primarily determined by the number of electrons in the shell. This is seen most clearly for HfO$_2$, where the contribution of the filled Hf-4f shell with 14 electrons crosses over that of the O-2p shell. HfO$_2$ contributions from K, L and M electrons have been bundled for clarity. At low energies that contribution lies more than two orders of magnitude below that of the O-2p electrons, but at high energies it approaches O-2p and Hf-4f.

Similar conclusions emerge from graphs (not shown) for the remaining oxides entering Figure 1.
Figure 5: Scaled stopping cross sections of H ions in oxides. a: $S$ per per oxygen atom, straight Bragg. b: $S$ per per oxygen atom, compound. c: Same excluding projectile excitation. d: $S$ per target electron, compound.
Figure 6: Same as Figure 5 for He ions.
5. Scaling

Roth et al. [3] concluded from their measurements as well as theoretical arguments that the stopping cross sections studied in their measurements are dominated by O-2p electrons. A plot of measured stopping cross sections per oxygen atom seemed to confirm this assertion, although ZnO did not fit into that picture.

Figure 5 shows a test of this assertion on stopping cross sections calculated by PASS. Scaling is evidently poor for the straight-Bragg option, as was found already in ref. [3] on the basis of experimental data. Figure 5b shows scaling for four materials in the low-energy regime, while Al₂O₃ and VO₂ fall outside. In view of a noticeable contribution from projectile excitation to stopping it makes sense to plot stopping cross sections excluding projectile excitation. The result is shown in Figure 5c, which shows perfect scaling within 10-15%. This is entirely within the accuracy of the PASS code.

Interestingly, scaling does not get lost completely at high energies, where the heavier oxides, HfO₂, ZnO and Ta₂O₅, form a bundle, as do the lighter oxides VO₂, Al₂O₃ and SiO₂.

Figure 5d shows the stopping cross section per target electron excluding projectile excitation. As mentioned above, curves meet here at the high-energy end. Interestingly, however, two bundles appear at low energies, and the division into bundles is the same as in Figure 5c.

The question may be asked why the stopping cross section of ZnO fits well into Figures 5b and 5c, while a major discrepancy was found in the experimental data [3]. PASS results for ZnO do not show any singular feature of ZnO as compared to other materials. At present we do not have a derivation of this scaling relation from first principles. However, the experimental data in Figure 1 show a particularly steep slope for ZnO, indicating either an anomaly in the stopping cross section or in the analysis.

Figure 6 shows the equivalent of Figure 5 for He ions. While the qualitative picture is the same, scaling appears more convincing in Figure 5c than in 6c. Searching for an explanation of this observation we produced a plot (not shown) analogous to Figure 4, right graph. While the qualitative picture is the same in the two graphs, there is a single distinct difference: The contribution from the Hf-5p shell, which is very close to the one from the O-2s shell for H, is about 20% higher for He. This increases the relative importance of Hf and, hence, the stopping cross section per oxygen atom. We also note that projectile excitation becomes increasingly significant as Z₁ increases. Thus, on the basis of the PASS code it is not obvious whether the scaling property expressed by Figure 5c reflects
6. Discussion

Several theoretical schemes have become available to calculate stopping parameters beyond the Born approximation from first principles, beginning with density functional calculations of low-energy stopping in a free-electron gas [15]. Limitations in terms of accuracy, covered energy range and ion-target combinations are set mainly by available computer capacity. The present calculations have been performed under the assumption that from a cost-benefit point of view, model calculations like the ones made here will remain useful for quite a few years.

The selection of ion-target combinations has been limited to systems where experimental data are available. Just as in case of elemental target materials, more experimental data exist for H and He than for any other ion. H ions are of particular interest, since Roth et al. [3] have offered a systematic study for six materials on one and the same apparatus.

On the other hand, PASS has been developed primarily for heavy ions and has only occasionally been applied to light ions [8, 16]. While PASS has shown to match experimental values for antiprotons well [8], the charge-state model applied in PASS is not optimal for H and He ions, although that should not be a major problem for $v \ll v_0$.

Moreover, there is some doubt about the validity of experimental low-energy stopping data because of the role of the neglected dependence of electronic stopping on the impact parameter in the analysis [10].

Figure 7 shows data for elemental solids that can be compared with the oxide data in Figure 1. Except for Al/Al$_2$O$_3$, graphs for elements look similar to those for oxides. As regards the low-energy regime, experimental data lie near or below the PASS results. This emplyes that discrepancies may in part be due to data analysis ignoring impact-parameter dependence of electronic stopping [10].

Considering all these reservations we pay attention primarily to the difference between the reported three ways to calculate stopping cross sections for oxides and the four approaches to a possible scaling relation.

Figures 1-3 show differences up to a factor of two in PASS output between the straight-Bragg and compound options for H ions. They reduce to 20-30% for He and down to $\sim$ 10% for Cl ions. These differences remain fairly constant up to the stopping maximum, where they start decreasing. A small constant difference is found for $E \gtrsim 10$ MeV/u, which follows from the change of the $I$-value in the Bethe logarithm [17, 18].
Figure 7: Stopping cross sections for H ions in 6 elemental solids. Experimental data compiled and referred to in ref. [6]. Lines found from PASS with same input as straight Bragg for oxides.
Of the four attempts to find a scaling relation, Figure 5c appears most convincing, both from the underlying physics and the result. Unfortunately it appears difficult to produce that particular plot on the basis of experimental data, since measurements of energy loss do not distinguish between target and projectile losses. However, this plot is a clear manifestation that the main contribution to electronic stopping has been identified. That conclusion has been arrived at in ref. [3] on the basis of a plot equivalent to Figure 5b using experimental data.

One may ask to what degree our reported procedure and results can be generalized. Since we have shown data for oxides of widely different masses and stoichiometry, we expect predictions of similar quality for other oxides. Since errors due to application of Bragg’s rule diminish with increasing $Z_1$, surprises are neither expected for heavier ions nor for ions in the Bethe stopping regime.

Although we do not see obstacles in applying the procedure to nitrides and chlorides and other inorganic compounds, we have focused on oxides, since the number of available data sets, although small and incomplete, allows looking for some systematics.

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