Electronic stopping of slow protons in oxides

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The energy loss of ions in matter has been under close investigation for many decades. In this field of research, profound knowledge about ion-target interactions is obtained. Data on the deceleration of ions in solids are useful in many fields like material science (ion beam analytics) or medicine (radiation therapy).

Kinetic energy of the projectile is transferred to the target due to two distinct processes: either by repulsive Coulomb interaction with the nuclei (nuclear stopping) or by excitation of electrons (electronic stopping). The mean energy loss per path length due to interaction with electrons is given by the electronic stopping power $S = dE/dx$. In order to eliminate the density dependence of S, often the electronic stopping cross section $\varepsilon = 1/n\,S$ is used, where n denotes the atomic density. While in the area of high energy ions (~ MeV energy) the behavior of the electronic stopping power is well understood for many materials, there still persist many unanswered questions for low energy ions (~ keV energy).

In the regime of low-energy ion scattering (LEIS), i.e. for primary ion energies from 0.5 to 10 keV, theory predicts that for a free electron gas (FEG) $S \propto v$, if the projectile velocity v is sufficiently low compared to the Fermi velocity v_F of the target electrons [1, 2]. The linear velocity dependence has been found also experimentally for protons in a FEG-like metal, as e.g. Al, [3, 4]. However, it has been shown that the band structure of the sample can strongly alter the velocity dependence of S: for noble metals like Cu, Ag or Au S shows a change in its velocity dependence correlated with the excitation of d-band electrons, located several eV below the Fermi energy [5, 6, 7]. For large band gap materials, e.g., KCl and LiF, electronic energy loss vanishes for ions slower than a certain threshold velocity v_{th} [8, 9]. A comparison to a TD-DFT calculation of electronic stopping of H^+ in LiF [10] shows that the experimental value of v_{th} is lower by a factor of 2. This suggests that for ionic crystals there may exist different energy loss channels in addition to electron-hole pair excitation. In order to close the gap between metals and insulators, oxides are perfect candidates: they feature band gaps of different sizes giving rise to either semiconducting or insulating properties.

In this contribution, we present low-velocity electronic stopping cross sections of protons in ZnO, VO_2, Ta_2O_5 and HfO_2. In case of VO_2, electronic stopping was measured in both, the semiconducting and the metallic phase (above 67 °C sample temperature). The results are

compared to earlier measurements of SiO_2 [8] and Al_2O_3 [11]. This selection permits to evaluate the electronic energy loss of oxides featuring band gaps between 0 eV (VO_2 in metallic phase) and ~ 9 eV (SiO_2). In order to look how the band structure is correlated with the electronic energy loss, DFT calculations of the electronic density of states (DOS) were performed.
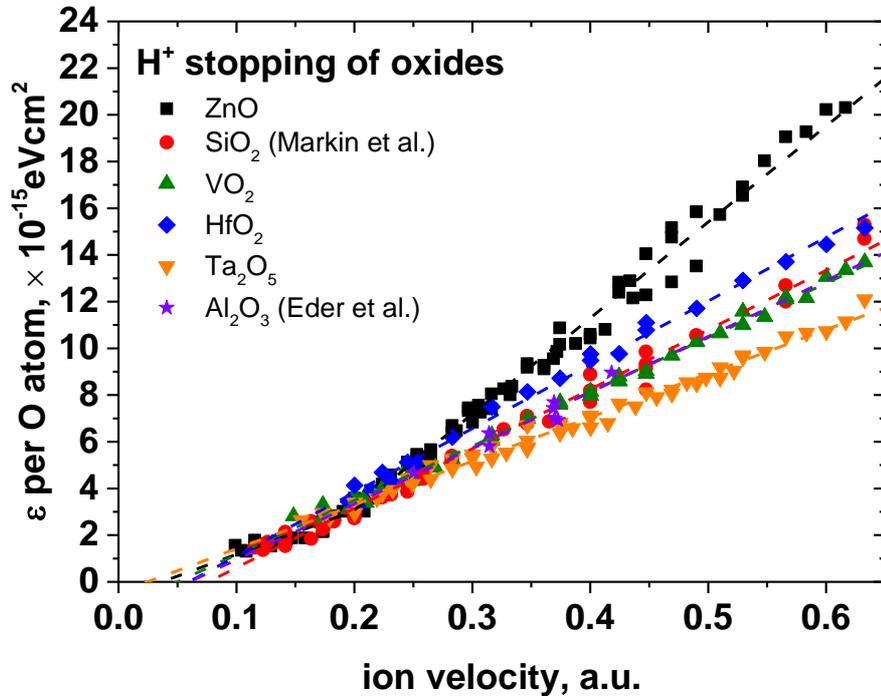
Fig. 1: H$^+$ electronic stopping cross sections per O atom of ZnO, SiO₂, VO₂, HfO₂, Al₂O₃ and Ta₂O₅ are shown as a function of ion velocity in atomic units. At very low ion velocities (v< 0.5 a.u.) electronic energy loss in all oxides coincides in efficiency.

For oxides it seems reasonable to characterize the stopping behavior in terms of ε per molecule, since the molecule comprises all valence electrons. To compare the stopping efficiency for the same number of valence electrons, it makes sense to divide the ε per molecule by the abundance of O in the molecule. In Fig. 1 this quantity is presented for ZnO, SiO_2, VO_2, HfO_2, Al_2O_3 and Ta_2O_5 as a function of the ion velocity in atomic units v/v_0, where $v_0 = c/137$ is the Bohr velocity. At $v < 0.25$ a.u., i.e., for $E < 1.5$ keV, for all oxides the electronic stopping cross sections per oxygen atom coincide. At $v > 0.25$ a.u. the electronic stopping cross sections of most oxides match within 10 %, with the exception of ZnO, where the contribution from d-band excitation results in a higher ε.

We will discuss to what extent properties like valence electron density (plasmon energy), electronic structure, band gap or effects like perturbation of the band structure by the ion (metallization) influence electronic stopping of protons in oxides.

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