A note on extracting electronic stopping from energy spectra of backscattered slow ions applying Bragg's rule

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ABSTRACT

Electronic stopping measurements in chemically reactive targets, e.g., transition and rare earth metals are challenging. These metals often contain low Z impurities, which contribute to electronic stopping. In this article, we present two ways how one can correct for the presence of impurities in the evaluation of proton and He stopping in Ni for primary energies between 1 and 100 keV, either considering or ignoring the contribution of the low Z impurities to multiple scattering. We find, that for protons either method leads to concordant results, but for heavier projectiles, e.g. He ions, the influence on multiple scattering must not be neglected.

1. Introduction

Ions propagating in matter lose energy due to interactions with the nuclei and the electrons of the target, i.e., by nuclear and electronic stopping. A measure for the mean energy loss per path length is the stopping power $S = dE/dx$. Alternatively, the stopping cross section ε (SCS) can be defined as $\varepsilon = 1/n \cdot dE/dx$, by taking into account the atomic or molecular density n of the target. In case of large ion velocities $v \gg v_F$, where v_F is the Fermi velocity, the deceleration of light ions is almost exclusively due to electronic stopping, which is well understood in this regime. At low velocities $v \leq v_F$, even light ions cause a significant perturbation of the electronic system of the target and therefore, screened Coulomb potentials and multiple scattering have to be considered. In this regime, both nuclear and electronic stopping contribute to the stopping power; the latter prevails for light ions and is mainly due to excitation of valence electrons. In many cases it is sufficient to describe the valence and conduction electrons of a solid as a free electron gas (FEG) [1], for which $S = Q(Z_1, n_s) \cdot v$ holds at $v \leq v_F$. Here, Q is the friction coefficient, which depends on the atomic number Z_1 and on the density of the FEG n_s [2]. Nonlinear calculations yield Q values for electronic stopping of slow ions in a FEG [3]. These Q values describe electronic stopping of protons in many metals and semiconductors accurately [4].

In the regime of high ion velocities, electronic stopping in compounds and the influence of impurities in any targets are accurately described by Bragg's rule [5]. For instance, the stopping power of a compound A_xB_y, is given by

$$S_{A_xB_y} = \frac{x \cdot S_A + y \cdot S_B}{x + y} \qquad (1)$$

with S_A and S_B being the electronic stopping power of the elements A and B, respectively. At low ion velocities, however, this approach is expected to be less accurate, since formation of a compound significantly modifies the states of the valence electrons. Deviations from Bragg's rule have been well documented in the literature, in particular for non-metallic compounds [6–9].

In order to perform accurate stopping measurements, samples of high purity are required. This request is particularly challenging for investigations of transition and rare earth metals, due to their high chemical reactivity and, consequently, the common presence of low Z impurities. For many elements, stopping data are available for only a limited energy range – commonly with a broad scatter of reported values [10,11]. Typically, the influence of impurities on electronic stopping is corrected by applying Bragg's rule. Note, that the presence of impurities will also affect nuclear stopping, as well as multiple scattering and, consequently, the path lengths of the projectiles. The present study focuses on possible ways to evaluate the electronic stopping power of slow protons in an exemplary case, i.e., Ni samples, in the presence of light impurities, from energy spectra of backscattered projectiles. We will discuss the impact of ion energy and species on the accuracy of the employed corrections. This analysis is done by comparing experimental spectra with Monte-Carlo (MC) computer simulations using different models.

2. Experiment

Three different sets of samples have been investigated: nm films of Ni on Si, (1) prepared ex-situ by e-beam evaporation under high vacuum conditions as well as (2) films prepared by in-situ evaporation using an Omicron EFM-3T evaporation system in ultra-high vacuum (UHV), and (3) a thick Ni sheet of high purity. It is preferable to deposit the Ni films on low Z materials, in order to exclude overlap of the signals. The samples have been characterized by time-of-flight elastic recoil detection analysis (ToF-ERD) at Uppsala University (UU), as well as by X-ray photo electron spectroscopy (XPS) and Auger electron spectroscopy (AES) at Johannes Kepler University Linz (JKU). From the ERD measurements a composition depth profile of the sample for the outermost ~500 nm was obtained, with a depth resolution of ~40 nm. In comparison, AES and XPS were used for surface analysis with an information depth of ~2 nm. Additionally, a combination of Ar bombardment and XPS was used to obtain a depth profile. This latter procedure gives information on surface and bulk contaminations as well as the chemical state of the Ni atoms.

The Ni film thicknesses (in terms of Ni atoms/cm^2) were determined via Rutherford backscattering spectrometry (RBS), for which the penetration depth (1–2 μm) is much larger than the investigated film thicknesses. The advantage of using areal densities is that the number of Ni atoms per area is determined independent of light bulk or surface contaminations like H, C, N or O [12]. In comparison, the mean penetration depth of protons and He ions at a primary energy of 8 keV in Ni is 55 nm and 35 nm, respectively.

For the Ni films, the energy loss measurements were performed without any pretreatment of the samples. The Ni sheet, which showed only surface and no bulk contaminations according to the ToF-ERD measurement, has been sputter cleaned to remove the surface oxide, by use of 3 keV Ar$^+$ ions in the UHV setup ACOLISSA (base pressure 5×10^{-10} mbar) at the IEP-AOP in Linz [13]. From AES the presence of only a sub-monolayer of oxygen was deduced. This surface contamination does not affect the energy loss measurements noticeably as for thick sheets the height of the spectra at an energy slightly below the high-energy edge is evaluated, where the signal is due to bulk Ni only. Protons, deuterons and He ions in the energy range of 0.5 keV to 10 keV were used as projectiles and hit the target at normal incidence. Both, scattered neutrals and positive ions were detected by a time-of-flight detector at a backscattering angle ϑ of 129°.

According to the XPS analysis the ex-situ prepared Ni film contains 10% C and 2% O as impurities, in addition to 88% Ni, which has been proved to be in the metallic state. Consequently, ignoring impurities in the target, the evaluation of ε_{Ni} will result in a too high value for the experimental SCS ε_{expt} (see Eq. (1)).

3. Monte-Carlo simulations and data evaluation

At low energies, scattering cross sections are large, leading to pronounced multiple scattering [14,15], and, consequently, to an increase in nuclear stopping and in path length of the projectiles. To properly take multiple scattering into account, the experimental energy spectra of backscattered ions are compared to MC simulations using the TRBS code [16]. This code permits to disentangle contributions from nuclear and electronic stopping as well as from the increase in path length. Nuclear collisions are described by the ZBL potential [17] and electronic stopping can be tuned in a way that agreement between simulated and experimental spectra is achieved.

Since different sample types (nm film and bulk) feature distinct energy spectra, different evaluation strategies for the electronic SCS are required. Spectra were recorded both for the thick Ni sheet as well as a reference (R) with known SCS, for the same number of incident ions. From the height ratio, H_R/H_{Ni}, the stopping ratio, $[\varepsilon_{Ni}]/[\varepsilon_R]$, can be evaluated: within the single scattering approximation, $H_R/H_{Ni} \propto [\varepsilon_{Ni}]/[\varepsilon_R]$ holds, so that ε_{Ni} can be evaluated since ε_R is known [18]. In the presence of multiple scattering,

there is no unambiguous way to relate spectrum height to electronic stopping. Therefore, we use ε_{Ni} as the only free parameter, which is optimized to reach optimum agreement between measured and simulated height ratios [19]. To minimize uncertainties in the scattering potential and, consequently, in the scattering cross section in the simulations, the reference is chosen to be of similar atomic number as the sample of interest; in this investigation Cu has been used [20]. For the stopping cross section of the reference ε_{Cu} was taken from [21], where data were measured for a clean Cu film on Si.

In the case of the thin Ni films, ε_{Ni} is determined from the width of the Ni peak in the energy spectra, which is related to both the electronic stopping and the thickness of the target, where the latter is obtained from RBS in terms of areal density. For the ex-situ grown films two different approaches to correct for the low Z impurities have been used. First, an a posteriori Bragg's rule correction was performed: energy spectra were simulated (for the areal thickness resulting from RBS) only considering the Ni atoms in the film (14 nm). Afterwards, the resulting stopping, S_{expt}, was corrected for the light impurities via $S_{Ni} = S_{expt} - S_O \cdot c_O/c_{Ni} - S_C \cdot c_C/c_{Ni}$, where c_{Ni}, c_O and c_C are the atomic concentrations of Ni, O and C, respectively. The electronic stopping powers of oxygen, S_O, and carbon, S_C, have been taken from SRIM2013 [22]. Note, however, that the SRIM data are an extrapolation or interpolation depending on availability of existing stopping data, and therefore, a potential source of uncertainty. The main advantage of this method is its a posteriori applicability, by performing data evaluation and simulation under the assumption of no impurities in the film. However, this approach neglects the influence of impurities in multiple scattering and the resulting changes in the path length of the projectiles in the sample, as well as their influence on nuclear stopping. Furthermore, the subtraction of contributions of light elements which have not been considered in the simulation is in conflict with conservation of the areal density of target atoms considering the equation given above. In the limit of low concentrations of impurities, the expected systematic inaccuracy is small. However, for decreasing energies, increasing concentrations of contaminations, and increasing atomic number of projectile and impurities an increasing discrepancy can be expected. Therefore, as a more elaborate approach a correction fully consistent with Bragg's rule has been performed: in this case the simulation was carried out with the proper stoichiometry as obtained from the XPS evaluation. In this case, also the influence of impurities on nuclear stopping and multiple scattering is considered in the simulation. Additionally, the film thickness was modified accordingly to ensure an equal number of Ni atoms as obtained from the RBS measurement (15.9 nm). In order to be able to compare the evaluated stopping powers of the two approaches one also has to ensure the same atomic Ni density in both evaluations. After obtaining an experimental stopping value for the contaminated film, Bragg's rule [5] according to the original definition can be applied: $S_{Ni} = (S_{expt} - S_O \cdot c_O - S_C \cdot c_C)/c_{Ni}$. Note, however, that Bragg's rule does not always yield reliable results as stated above, e.g., if the investigated sample has a significant change in the density of states, as it is the case for oxides, but not the case for the present samples as indicated by the XPS data. In this contribution we implement the two approaches for correction as presented above as a method applicable for samples with a small amount of low Z impurities. In the present study, the influence of the impurities on the stopping data without correction is below 15%.

4. Results and discussion

An experimental energy spectrum obtained for 8 keV He ions scattered from the ex-situ Ni film on Si is shown in Fig. 1. For comparison two different TRBS simulations according to both approaches as introduced above are presented. Good agreement between experiment and simulations according to both corrections can be achieved. Note, that the simulated spectra have been convoluted with a Gaussian (FWHM ~400 eV) in order to take the experimental resolution into