

# Charge exchange between He<sup>+</sup> ions and solid targets: The dependence on target electronic structure revisited

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## ABSTRACT

This work compares the charge exchange properties of a large set of pure elemental solid targets by studying the neutralisation and reionisation in low-energy ion scattering (LEIS) experiments with He<sup>+</sup> as incident ion. Neutralisation is extracted from the characteristic velocity in inverse velocity plots, while reionisation of neutralised He scattered on sub-surface atoms is studied through the threshold energy and intensity of so-called tails in LEIS spectra. Our work qualitatively reproduces the previously reported systematic dependence of neutralisation probability versus group (column) in the periodic table. However, such a trend is not observed for the reionisation probability, which is in contradiction to previously published results on neutral He backscattering. The results are discussed in terms of the electronic structure of transition metals and charge exchange in close collision.

## 1. Introduction

Low-energy ion scattering (LEIS) is an important analysis technique for studying the composition of the surface of materials. When noble gas ions are used as primary ion species and the backscattered ions are studied with an electrostatic energy analyser, distinct surface peaks are observed that correspond to ions that were backscattered by outermost surface atoms [1,2]. Ions that penetrate the target beyond the first monolayer are efficiently neutralised, but may still be backscattered by atoms in deeper layers and have a finite probability to be reionised by surface atoms before leaving the surface. These reionised ions have lost energy due to inelastic reionisation processes [3], as well as electronic and nuclear stopping on their pathway through the material [4,5] and therefore contribute to a so-called tail signal on the low energy side of the surface peak. When the stopping power of the investigated material is known, this tail signal can be used for non-destructive investigation of the depth profile of elements or determination of layer thicknesses with sub-nm resolution, as has been demonstrated for e.g. Mo/Si diffusion studies [6], self-assembled monolayers on Au [7], atomic layer deposition films used in the semiconductor industry [8,9], magnetron deposited films with nm thickness range [10,11] and growth of oxide films on metals [12].

Apart from causing tail signals, reionisation may also lead to broadening or splitting of the surface peaks in a LEIS spectrum, in case

an incoming He<sup>+</sup> backscatters on a surface atom and undergoes neutralisation followed by reionisation. Since reionisation is an inelastic process, the surface peak of such a reionised He particle will appear ~20 eV (a typical ionisation energy threshold) lower compared to a He<sup>+</sup> ion that did not undergo neutralisation during the scattering event. This splitting of the LEIS surface peak has indeed been observed for scattering with very low (<0.5 keV) energy ions, where the intrinsic width of the surface peaks is small [3]. For few keV He<sup>+</sup> scattering the surface peaks are intrinsically broad compared to the ionisation energy, but it has been confirmed that elements for which reionisation of He is important, generally show broader LEIS surface peaks [13]. Knowledge of charge exchange processes is thus important for understanding the shape of LEIS surface peaks and the quantification of LEIS spectra, which involves knowledge of the ion fraction.

Before discussing previously reported systematic studies of charge exchange properties for larger series of target atoms, we briefly summarise the processes involved in charge exchange of noble gas atoms interacting with solid targets. When a He<sup>+</sup> ion is within electron tunnelling distance from a target atom, electron transfer from the target atom to the ion is possible through an Auger process. This process is only allowed when the electron level in the target has a lower binding energy compared to the He 1s energy level (location of the electron hole in a He<sup>+</sup> ion). The excess energy is used for exciting a plasmon in the target or emission of an Auger electron. Auger charge transfer processes under

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normal conditions only result in neutralisation of the noble gas ion and therefore do not need to be considered for understanding reionisation [2]. Reionisation of neutral He by interaction with a target atom is possible through (i) (quasi-)resonant charge exchange and (ii) collision-induced processes [2]. (Quasi-)resonant charge exchange is possible whenever one or more energy levels of the ground state or excited states of the He atom align with energy levels of bound states or the valence band of the target. Since in a scattering event the He particle approaches the target atom to sub-Ångström distances, the energy levels of the He<sup>+</sup> ion will be broadened and lifted (i.e. get closer to the vacuum level), such that resonant charge transfer processes in a collision process may be possible, even if the energy levels of He and the target atom do not fulfil resonant conditions at large distance. In addition to resonant charge exchange, collision-induced neutralisation or reionisation may happen when a He atom approaches a target atom within sub-Ångström distances. In collision-induced processes a quasi-molecular state of He with the target atom is formed, which involves occupation of anti-bonding electron states of the quasi-molecule [2,3]. In a schematic plot (see Fig. 3.4 in Ref. [2]) of total energy of the He + target atom (A) system vs. distance between both atoms, this is schematically indicated as a crossing of the curves of the He<sup>0</sup> + A state (where He is neutral) and the He<sup>+</sup> + A<sup>-</sup> state (where He is reionised) at a distance  $R_M$ . When in a scattering event the He atom approaches the target atom to  $R_M$  or closer, reionisation or neutralisation processes (depending on the initial charge state of He) can occur with high probability [2].

For a given scattering geometry, the distance of closest approach of incident particle and target atom is related to the initial energy of the incident particle. A higher initial energy results in a smaller distance of closest approach [1], which implies that a minimum energy is needed to approach the target atom  $R_M$  or closer. This is reflected in the so-called threshold energy for reionisation, or the minimum initial energy required for reionisation to occur. The existence of such a reionisation threshold has been demonstrated for backscattering of near-normally incident He neutrals with an energy range of ~0.2–2 keV [3,14,15], as well as for reionisation of sub-surface scattered He particles producing tails in LEIS spectra [2]. Even though the geometry of the He-target atom interaction leading to reionisation is quite different for both cases, the extracted reionisation thresholds for different elements by both methods follow globally the same trend, as will be discussed in more detail in Section 4.1.

Souda et al. systematically studied the He reionisation properties of a large set of elements by backscattering of He neutrals [14,15]. They found that the reionisation probability shows a characteristic ‘v shape’ when plotted versus their group or column in the periodic table. These results were explained in terms of the filling of d electron bands of the transition metals influencing the possibility of charge transfer in close collision. Mikhailov et al. did a similar study on He<sup>+</sup> neutralisation and concluded that reionisation and neutralisation probability are closely interlinked [13]. To our knowledge, there is not such a systematic study for the reionisation probability of various elements based on LEIS tail signals. In this paper we provide such a systematic analysis and compare our results to those of Souda et al. Based on our analysis, we conclude that the reionisation probability of 3 keV incident He<sup>+</sup> ions, as typically used for LEIS tail analysis with modern LEIS equipment, does not follow the trend found by Souda et al. A comparison with He<sup>+</sup> neutralisation measurements on a subset of these materials in our laboratory shows that Souda et al. most likely underestimated the influence of the ion fraction of LEIS experiments used as reference for their reionisation measurements. This means that the conclusion that neutralisation and reionisation are closely linked, should be revised.

In the next section, we discuss the theory needed to quantitatively compare reionisation and neutralisation by different elements based on the signal from LEIS tails and surface peaks. Next, we discuss the experimental approach and provide an overview of the various sources of reionisation and neutralisation data from our laboratory and literature sources that are discussed in this paper. This is followed by a

systematic analysis of the reionisation and neutralisation properties of elements versus their group in the periodic table. These results are then discussed in comparison with the systematic studies by Souda et al. [14,15] and Mikhailov et al. [13].

## 2. Theory

### 2.1. LEIS surface peak quantification

In LEIS experiments, the signal of scattered ions is commonly measured as a yield expressed in detected counts  $\mathcal{S}_i$  divided by the incident primary ion dose or fluence (units of counts divided by the product of primary beam current  $I_p$  and measurement time  $t$ ). In this way, the LEIS yield  $Y_i$  for a surface peak of element  $i$  can be expressed as [2]:

$$Y_i = \frac{\mathcal{S}_i}{I_p t} = \frac{1}{e} \xi P_i^+ \frac{d\sigma_i}{d\Omega} N_{i,\text{area}} \quad (1)$$

with  $e$  the elementary charge,  $\xi$  the analyser sensitivity,  $P_i^+$  the ion fraction for scattering on element  $i$ ,  $d\sigma_i/d\Omega$  the (energy dependent) differential scattering cross-section for scattering on element  $i$  and  $N_{i,\text{area}}$  the areal density of atoms  $i$  on the surface of the target. It should be noted that in this expression the opening angle of the detector is incorporated in the analyser sensitivity factor  $\xi$ , which has units of solid angle. In this work we used scattering cross-sections calculated according to the Thomas-Fermi-Molière potential [1,16], following the approach by Mikhailov et al. [13]. The ion fraction can be expressed in terms of the characteristic velocity for neutralisation  $v_c$  according to [2]:

$$P_i^+ = e^{-\frac{v_c}{v_{\perp,\text{in}} - v_{\perp,\text{out}}}} = e^{-\frac{v_c}{v_{\perp}}} \quad (2)$$

where the reciprocal perpendicular velocity  $1/v_{\perp}$  is defined as  $1/v_{\perp,\text{in}} + 1/v_{\perp,\text{out}}$ , with  $v_{\perp,\text{in(out)}}$  the component of the ion velocity perpendicular to the surface plane along the incoming (outgoing) path. This expression is based on the assumption that the charge exchange between target and ion can be expressed as an average charge transfer rate. A higher perpendicular velocity component implies that the ion is for a shorter time in the vicinity of the target (where charge transfer can occur), resulting in a higher fraction of survived ions.

The characteristic velocity can be determined from measurements of the surface peak signal for a range of primary energies, by plotting the natural logarithm of the yield divided by the scattering cross-section against the reciprocal velocity:

$$\ln \left( \frac{Y_i}{\frac{d\sigma}{d\Omega}} \right) = \ln(\text{const.} \cdot N_i) - \frac{v_c}{v_{\perp}} \quad (3)$$

yielding a linear relationship with slope  $-v_c$ . In this expression all factors related to detector sensitivity are incorporated in a constant. The characteristic velocity thus offers the possibility to compare the neutralisation behaviour of different elements, since  $v_c$  is in principle independent of other factors influencing the LEIS yield (scattering cross-section, surface atomic density and instrumental sensitivity). It should be noted, though, that the charge transfer rates in some cases may depend on the local environment of the atom on which the ion scatters. It has been reported that for scattering on single crystals,  $v_c$  may depend on surface crystalline orientation and scattering geometry [17,18], due to influence of electronic structure on charge transfer. Also, changes in valence band structure and/or presence of non-local valence band states may depend on the chemical surrounding of an atom, thereby influencing charge transfer and  $v_c$ , which is commonly expressed as a matrix effect of chemical surrounding on the ion fraction [19–23]. For this reason, we only compare pure elements in this study. Since surfaces are prepared by sputtering (without annealing) and the employed analyser integrates the LEIS signal over the full azimuthal angle, we assume that

crystal orientation or surface structure effects have no or limited influence on the outcome of our study.

## 2.2. LEIS tail quantification

Analogously to Eq. (1), an expression can be formulated for the LEIS tail signal  $H_i$ . The tail signal represents the depth distribution of element  $i$ , therefore the signal within a certain detector energy window  $\Delta E$  can be attributed to backscattering on atoms in a certain slab thickness  $d_s$  in the sample. The slab thickness is related to the energy window through the relation  $d_s = \Delta E/S_i$ , with  $S_i$  the (energy dependent) stopping power of material  $i$  in units of energy loss per unit length. The areal density of atoms contributing to the tail signal in the energy window is thus given by  $d_s N_{i,\text{vol}}$ , with  $N_{i,\text{vol}}$  the volume atomic density of atoms in the material. In this way,  $H_i$  can be expressed as [6,24]:

$$H_i = \frac{\mathcal{J}_{\text{tail}}}{I_p t} = \frac{1}{e} \xi N_{i,\text{vol}} \frac{\Delta E}{S_i} \frac{d\sigma_i}{d\Omega} R_i^+ \quad (4)$$

with  $\mathcal{J}_{\text{tail}}$  the absolute signal in the energy window in number of counts and  $R_i^+$  the probability of reionisation, i.e. the probability that a He particle backscattered by a target atom in the considered slab thickness into the acceptance area of the detector will be reionised by interaction with a surface atom when leaving the sample. Even though stopping values can be estimated, e.g. through SRIM software [25], the reionisation probability of different materials cannot be as readily compared between different materials as the characteristic velocity for neutralisation, since  $R_i^+$  both depends on the surface atomic density and the probability of reionisation in a single He surface atom interaction [6]. We therefore propose to express the dimensionless term  $R_i^+$  as  $\sigma_{R,i} \cdot N_{i,\text{area}}$ , where  $\sigma_{R,i}$  is defined as (energy dependent) reionisation cross section (in units of area) for surface atoms  $i$ . The reionisation properties of different elements can thus be compared by evaluating the measured tail height according to:

$$\sigma_{R,i} = \text{const.} \cdot H_i \frac{1}{N_{i,\text{vol}}} \frac{1}{N_{i,\text{area}}} \frac{S_i}{\frac{d\Omega}{d\Omega}} \quad (5)$$

where all factors related to detector efficiency and settings ( $\xi$  and  $\Delta E$ ) are incorporated in a constant. At first glance it may seem incorrect that the density of the material appears in Eq. (5) twice (once as volume density and once as area density). However, one should keep in mind that in general the sub-surface atoms on which He backscatters and the surface atoms causing reionisation should not necessarily be the same material, which explains that both densities should be taken into account.

In these expressions for the tail height we neglected the fact that for keV range particles, the exact dependence of scattered particle signal vs. final energy depends on the multiple scattering trajectories inside the target. A more accurate way to take this into account, would be the use of so-called TRBS simulations [4,26,27]. These simulations take into account multiple scattering trajectories by performing Monte Carlo simulations of the interaction of many ions with a target. Such simulations can only be reliably performed when the electronic stopping correction factors are known, which is not the case for all elements studied. Therefore we consider this beyond the scope of this work. In order to exclude the possible influence of multiple scattering trajectories as much as possible, we only consider the tail height at a single energy, just below the LEIS surface peak.

## 3. Materials and methods

Samples studied in this work and in our laboratory were either foils with  $\geq 99.9\%$  purity, wafer pieces or thick ( $> 20$  nm) films deposited by direct current magnetron sputtering from targets with  $\geq 99.9\%$  purity. Since this work involves analysis of measurements not published so far, as well as a comparison with previously published data from our

laboratory and other literature references, Table 1 provides an overview of the elements, sample types, preparation method and relevant physical properties. Samples measured in our laboratory were cleaned from native oxide and hydrocarbon contamination by  $\text{Ar}^+$  ion sputtering, using a separate sputter gun incident at  $59^\circ$  with respect to the sample surface normal. For magnetron sputtered films 0.5 keV ions were used for cleaning, whereas foil samples were initially cleaned by 2 keV ions until the LEIS surface peak of the investigated elements saturated (i.e. did not increase upon further ion sputtering). The investigated Y film had a 10 nm Pd capping layer to protect the Y against oxidation. This Pd cap film was removed by ion sputtering in order to study the Y film. The Cu foil sample was subsequently cleaned by 5 keV  $\text{Ar}^+$  and 3 keV  $\text{Ne}^+$  sputtering at normal incidence (using the primary ion gun of the LEIS set-up). The preparation procedure for this sample is deviating because this measurement was carried out as part of an interlaboratory round robin study.

The calculation of (relative) reionisation cross-sections from LEIS tail signals requires knowledge of atomic density and stopping values. The atomic density was assumed to be equal to bulk values reported in Table 1, while the surface atomic density was approximated as  $N_{i,\text{vol}}^{2/3}$  (see ref. [28]). Stopping values (sum of nuclear and electronic stopping) were extracted from SRIM software [25].

LEIS spectra were acquired with a high sensitivity LEIS spectrometer of the type Qtac<sup>100</sup> supplied by IONTOF GmbH (Münster, Germany). In this spectrometer samples are probed with a normally incident ion beam ( $^4\text{He}^+$  for the present study) at a fixed scattering angle of  $145^\circ$ , with an opening angle of the detector of  $\pm 1^\circ$ . In order to enhance the sensitivity, the detector integrates the signal along the full azimuthal range. The primary beam current, typically around 3 nA, was measured with a Faraday cup directly before the LEIS measurement. The analysis area was set to  $1 \times 1$  mm<sup>2</sup> by rastering the ion beam and a typical fluence around  $2\text{--}3 \times 10^{14}$   $\text{He}^+$  ions/cm<sup>2</sup> was used for a single measurement. Comparison of tail heights was only performed for measurements with 3 keV primary ions, using an analyser pass energy of 3 keV to ensure that the detector settings were equal for all compared materials. For characteristic velocity measurements, LEIS spectra were obtained with primary ion energies in the range from 1 to 6 keV. In this case, primary energies above 4 keV require adaptation of the pass energy. It was verified that the influence of pass energy on the surface peak area (for the same primary energy) was small compared to the typical statistical variations between measurements.

## 4. Results

### 4.1. Reionisation threshold energy

In this section we systematically compare measured energy thresholds for He reionisation with values reported in literature before. Fig. 1 shows as example a LEIS spectrum acquired with 3 keV  $\text{He}^+$  ions on sputter cleaned Mo [22]. By linearly extrapolating the lower part of the tail signal to zero LEIS yield (red line), the threshold energy for reionisation  $E_{\text{th}}$  is obtained. Especially for light elements, the lower part of the tail may overlap with the low energy background due to sputtered samples atoms. Therefore, the linear extrapolation was only applied in an energy range where this sputter background has a minimal influence on the LEIS yield. It should be noted that the actual dependence of the tail signal versus energy is influenced by the reionisation and backscattering probability and therefore not *a priori* expected to be linear. The possible sputter background and the approximation of linear interpolation are therefore the main contributions to the error margin. LEIS spectra of other elements discussed in this work can be either found in references provided in Table 1, or in Figs. S1-S8 in the supplementary information (for spectra that were not published in previous publications by our group).

In Fig. 2 our reionisation threshold values from LEIS tails are compared with previously reported literature values for the threshold

**Table 1**

Overview of materials studied in this work, including reference results from literature used for comparison. Target type: MS indicates magnetron sputtered. Stopping values are extracted from SRIM software [25]. Atomic density and stopping value are only mentioned for samples for which these values were used for determining reionisation cross-sections from tail heights.  $v_c$  is the characteristic velocity for neutralisation of  $\text{He}^+$ . Mikhailov et al. reported  $v_c$  values relative to Pd [13], these values have been converted to absolute values by reading the  $v_c$  value of Pd from the graph in this reference. Similarly the  $v_c$  values for Ge [29] and In [30] were not reported in the original publications, but have been extracted from published graphs. Samples measured in our laboratory are listed with XUV in the column reference (s).

element	$N_{i,\text{vol}} (\times 10^{22} \text{ atoms/cm}^3)$	target type	preparation	stopping (eV/nm)	$v_c (\times 10^5 \text{ m/s})$	reference(s)
Ag		(110) crystal	sputtering + annealing		1.20	[31]
Ag		(110) crystal	sputtering + annealing		1.20 1.62 1.73	values for different scattering geometries, [18]
Ag		(111) crystal	sputtering + annealing		1.40	[31]
Ag		Poly			1.39	[31]
Al		(111) crystal	sputtering + annealing		2.2	[32]
Al		(111) crystal	sputtering + annealing		2.4	[33]
Al		evaporated film	sputtering		3.3	[34]
Al	6.02	MS film	sputtering	55.0	2.1	XUV, [22]
Al		Poly	sputtering + annealing		3.8	[13]
Al		polycrystalline evaporated film	sputtering + annealing		2.5	[32]
Au		(110) crystal	sputtering + annealing		1.42	[18]
Au	5.90	Foil	sputtering	64.5		XUV, this work
Au		Poly			1.6	[31]
B		MS film	sputtering		2.15	XUV, [35]
C		HOPG	annealing		7.4	[20]
Ca		evaporated film	sputtering		2.6	[34]
Ce	2.87	MS film	sputtering	38.2		XUV
Cr		Poly	sputtering + annealing		3.7	[13]
Cu		(100) crystal	sputtering + annealing		1.62	[17]
Cu		(110) crystal	sputtering + annealing		1.18	[17]
Cu	8.45	Foil	sputtering	66.6	1.3	XUV, this work
Cu		Foil	sputtering		1.9	[34]
Cu	8.45	MS film	sputtering	66.6	1.19	XUV, this work
Cu		Poly	sputtering + annealing		2.0	[13]
Cu		polycrystalline	not explicitly specified		1.92	[36]
Ge		(100) wafer piece	sputtering + annealing		7.4	[29]
Hf	4.49	MS film	sputtering	43.4	1.6	XUV, [22]
In		polycrystalline evaporated film			4.9	[30]
Ir		Poly	sputtering + annealing		2.4	[13]
La	2.70	MS film	sputtering	41.8	3.1	XUV, [21]
Mo	6.42	MS film	sputtering	79.7	0.65	XUV, [22]
Mo		Poly	sputtering + annealing		3.8	[13]
Nb	5.56	MS film	sputtering	77.7	1.35	XUV, this work
Ni		(100) crystal	sputtering + annealing		1.8	[13]
Pd		Poly	sputtering + annealing		1.3	[13]
Pt		Poly	sputtering + annealing		1.5	[13]
Re		Poly	sputtering + annealing		3.2	[13]
Rh		Poly	sputtering + annealing		1.6	[13]
Ru	7.36	MS film	sputtering	67.9	0.71	XUV, [22,27]
Si	5.00	(100) wafer piece	sputtering	44.7	3.35	XUV, this work
Si		(100) wafer piece	sputtering + annealing		4.8	[13]
Si	5.00	MS film	sputtering	44.7		XUV, [10]
Ta		(111) crystal	sputtering + annealing		2.25	[33]

(continued on next page)

Table 1 (continued)

element	$N_{i,vol}$ ( $\times 10^{22}$ atoms/ $cm^3$ )	target type	preparation	stopping (eV/nm)	$v_c$ ( $\times 10^5$ m/s)	reference(s)
Ta	5.55	Foil	sputtering	72.8	1.2	XUV, this work
Ta		Poly	sputtering + annealing		3.4	
W	6.30	MS film	sputtering	74.5	3.8	XUV, [37]
W		Poly	sputtering + annealing			
Y	3.02	MS film with Pd cap layer	sputtering	36.3	1.39	XUV, this work

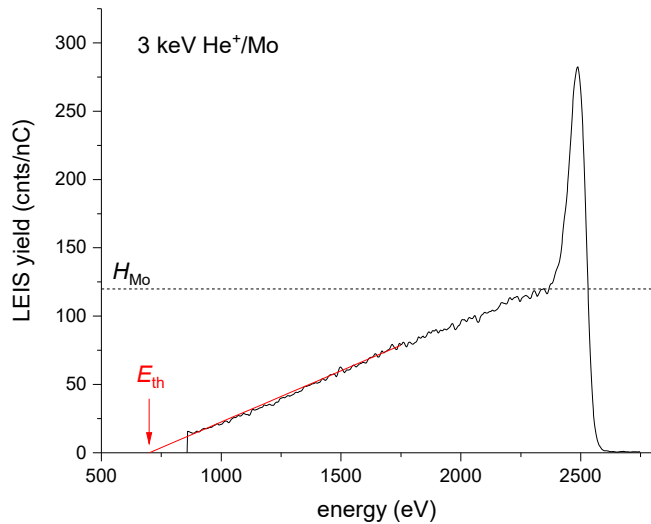


Fig. 1. 3 keV  $He^+$  LEIS measurement on Mo (black), with schematic indication of the tail height  $H$  just below the onset of the surface peak and the energy threshold for reionisation  $E_{th}$ , obtained by linear extrapolation of the low energy part of the tail (in red).

measured by neutral backscattering and LEIS tail signal extrapolation [2,3], with on the horizontal axis the group (column) in the periodic table of elements. A reionisation threshold  $>2000$  eV is displayed as

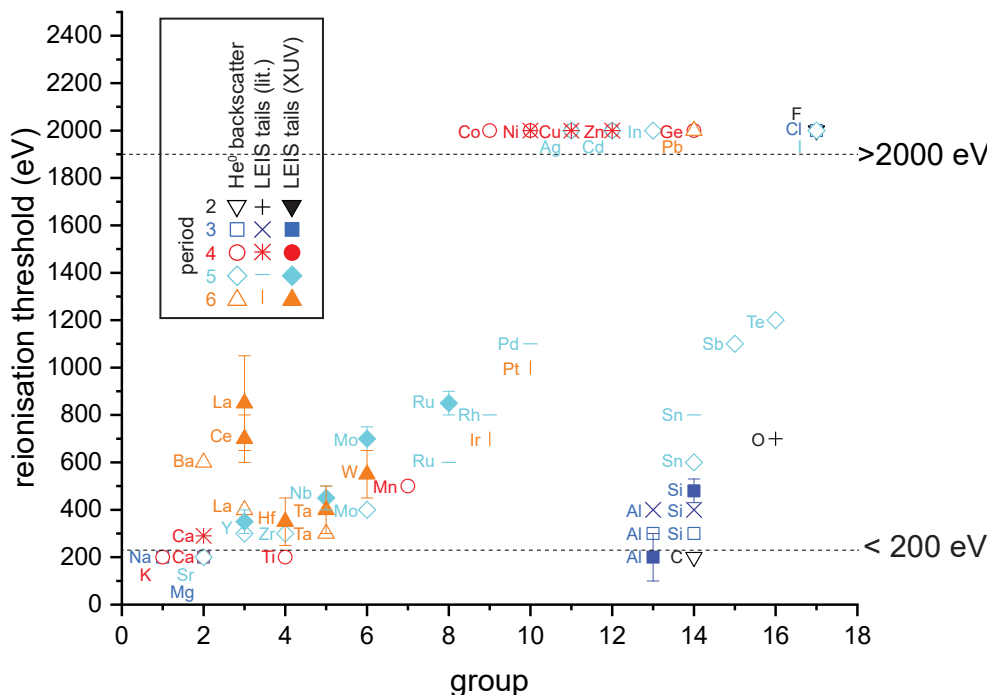


Fig. 2. Overview of reionisation threshold values versus group of the element in the periodic table. A value above the upper dashed line indicates that the threshold was reported to be  $>2000$  eV, a value below the lower dashed line indicates a threshold  $<200$  eV. Element labels are on the left-hand side of data points. Various symbols and colours indicate different periods (rows) in the periodic table according to the legend. Open symbols in the column with  $\nabla$  on top refer to literature values for reionisation by backscattering of  $He^0$  [2,3]. All symbols in the column with  $+$  on top correspond to literature values for the reionisation threshold from LEIS tails [2], filled symbols (column label XUV) are from LEIS tail measurements in our laboratory.

datapoint at 2000 eV, similarly a value  $\leq 200$  eV is displayed at 200 eV. In line with literature results for Cu, Au and Zn [2,38], no clear LEIS tail signals were observed for Cu and Au in our work, due to the high reionisation threshold. It should be noted that for those elements the existence of a (small) tail signal may be attributed to reionisation by contaminant species, such as oxygen or carbon [2,38]. The trend in this figure confirms previous observations in literature that for the transition metals (group 3–12) the reionisation threshold tends to increase with increasing filling of the d electron bands. The only exception to this trend are La and Ce, which are part of the lanthanides. Our values for the reionisation threshold are slightly higher than those reported in literature. In case of the reference LEIS studies, this deviation may be caused by the use of a different primary energy, since published spectra show a dependence of the extrapolated threshold value on primary energy [13,22]. A likely reason for this, is that the exact shape of the tail depends on the multiple scattering trajectories inside the sample, which are expected to be depending on the primary energy. For the neutral backscattering experiments of Aono and Souda et al. it can be expected that a lower reionisation threshold is found in comparison with LEIS tails, since the reionisation takes place in a high angle (typically  $160^\circ$ ) collision, while a LEIS tail signal typically involves a scattering event where a neutral backscattered deeper in the sample reionises in a low angle scattering event with a surface atom before leaving the sample. Since, for equal energy, a higher scattering angle involves closer approach to the target atom, it can be expected that the reionisation threshold energy is lower for a higher scattering angle.

#### 4.2. Reionisation cross-section from tail height

As next step to compare the reionisation probability of He by different elements more quantitatively, we compare the LEIS tail heights measured on different elements. In order to exclude the influence of multiple scattering on the tail shape as much as possible, we use the tail height  $H$  just below the onset of the surface scattering signal (as indicated in Fig. 1) as measure for the signal of reionised particles. 3 keV He<sup>+</sup> primary ions were used for this analysis, since for lower energies the surface peak will get closer to the reionisation threshold and the tail signal might be influenced by the signal of low energy sputtered atoms from the sample [2]. Since the intensity of the scattering signal is strongly influenced by scattering cross-section and density of the material, the reionisation probability is compared by plotting the reionisation cross-section calculated according to Eq. (5) versus the group number of the element, which yields the plot in Fig. 3. Since the absolute sensitivity of the LEIS detector (in terms of detected counts per incident ion) is not known, the reionisation cross-section are in arbitrary units. However, since all measurements were carried out with identical analyser settings, the results can be compared on a relative scale.

The results in Fig. 3 are quite distinct from the estimate of the reionisation probabilities reported by Souda et al. [15], which show a typical ‘v shape’ for which the reionisation probability is highest for elements on the left hand side of the periodic table, gradually decreases up to group 12, after which it again rises for elements more on the right hand side of the periodic table. The only similarity of our results compared to those of Souda et al., is a very low tail signal for Au and Cu. In the next section we will discuss the origin of these differences.

#### 4.3. Reionisation cross-section versus LEIS ion fraction

Publications on charge exchange between He and solid targets usually refer to the He<sup>0</sup> scattering results by Souda et al. as the “ionisation probability” of He<sup>0</sup>. However, Souda et al. describe these results in their original work [15] as an “estimate” of the ionisation probability. When quoting from their work, this estimate is described as: “We have estimated the ionization probability from the ratio of the normalized He<sup>+</sup> intensity for He<sup>0</sup> incidence to that for He<sup>+</sup> incidence,  $I^0/I^+$ .” How should this quantity exactly be interpreted? In a He<sup>0</sup> scattering experiment, the measured yield is a signal of detected ions divided by the incoming fluence of primary He<sup>0</sup> particles. Similarly to our LEIS tail heights, this signal cannot be readily compared for different target elements, due to differences in scattering cross-section and atomic density. From the description in the work of Souda et al., the influence of atomic density and cross-section was accounted for by dividing the ion yield of a He<sup>0</sup> scattering experiment on a specific target by the ion yield for a He<sup>+</sup>

scattering experiment on the same target, since the yield for He<sup>+</sup> scattering depends on scattering cross-section and atomic density in exactly the same way as for He<sup>0</sup> scattering. But if the ion fraction (or neutralisation probability) for He<sup>+</sup> scattering shows a systematic dependence on position in the periodic table (i.e. on electronic structure), the estimate of the reionisation probability calculated according to the method of Souda et al. will both reflect systematic variations of the ionisation probability of He<sup>0</sup> and neutralisation probability of He<sup>+</sup>. Since the systematic investigation of characteristic velocities for He<sup>+</sup> neutralisation by Mikhailov et al. [13] showed that the neutralisation probability has a similar ‘v shape’ dependence vs. the group number in the periodic table, this must mean that the estimate of the ionisation probability by Souda et al. is actually a combined quantity influenced by both the ionisation probability of He<sup>0</sup> and the neutralisation probability of He<sup>+</sup>.

We now combine results from tail height measurements and characteristic velocity measurements in our laboratory and show that in this way a similar trend in charge exchange properties as reported by Souda et al., can be reproduced. The numerator  $I^0$  in the quantity plotted by Souda et al. is proportional to the ionisation probability of He<sup>0</sup> and therefore should be proportional to  $\sigma_{R,i}$  calculated according to Eq. (5). The denominator  $I^+$  should be proportional to  $P_i^+ = \exp(-v_c/v_{i,1})$ . If we thus compare the ratio  $\sigma_{R,i}/P_i^+$  for different elements, one would expect a similar behaviour as reported by Souda et al., with the main difference that Souda’s results were reported for 1 keV He scattering and that in the case of He neutral scattering the reionisation takes place at a higher scattering angle compared to LEIS tails (as discussed before).

Fig. 4 compares Souda’s results of  $I^0/I^+$  (open symbols) [15] with  $\sigma_{R,i}/P_i^+$  (solid symbols) measured in our laboratory, based on 3 keV He<sup>+</sup> LEIS tails and  $v_c$  values listed in Table 1. This figure contains less LEIS based data compared to Fig. 3, since for several elements there is only 3 keV LEIS data available and no characteristic velocity data, which requires elaborate measurements at multiple primary energies. When previously published  $v_c$  values from our laboratory were used, the reference to the original data is provided in Table 1. For elements for which inverse velocity plots (measured in our group) were not already published, this data is included in the supplementary information (Figs. S9–S14).

Comparison of the estimate of the ionisation probability by Souda et al. to our data of the reionisation cross-section divided by LEIS ion fraction shows that this representation of our LEIS data reproduces the previously reported trend vs. group of the investigated elements within the typical scatter of Souda’s original data. Since our data on the reionisation cross-section in Fig. 3 shows no clear trend versus group number, while it has been reported by Mikhailov et al. that  $P^+$  does show a distinct ‘v shape’ versus group number [13], we conclude that the published “estimates of the ionisation probability” by Souda et al. must

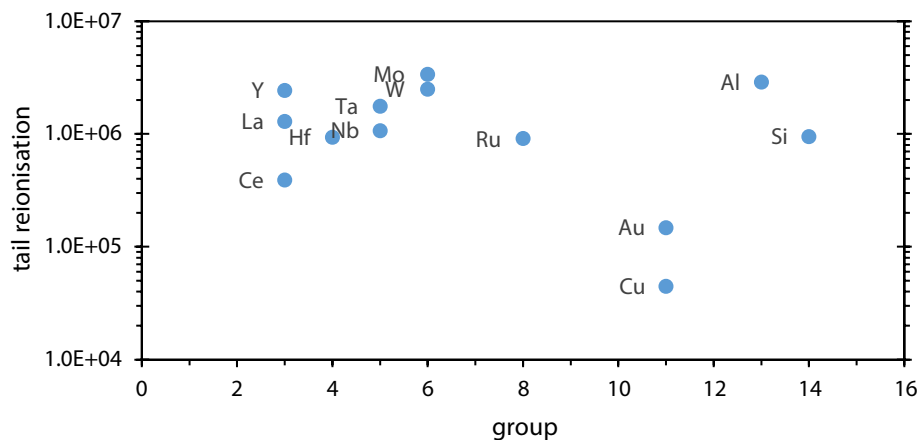
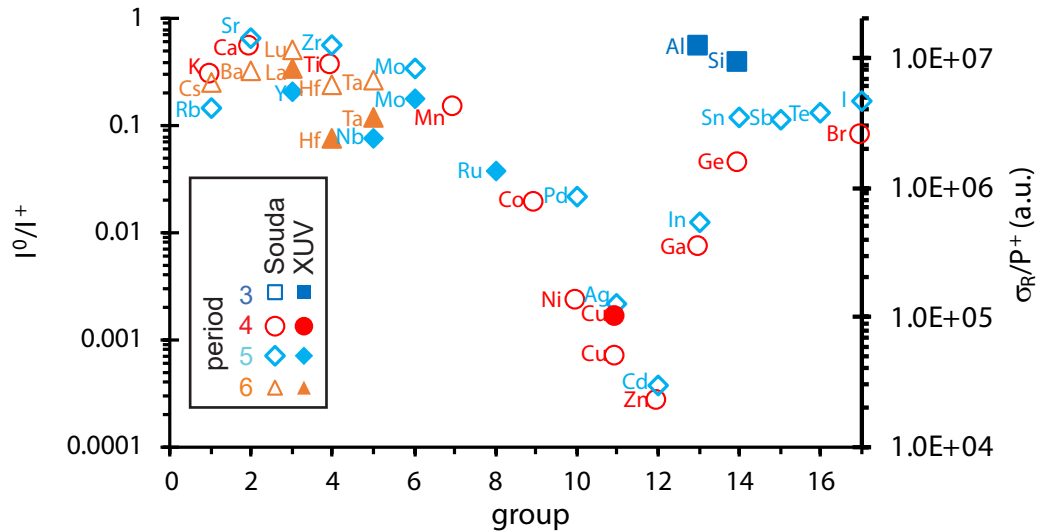


Fig. 3. LEIS tail reionisation cross-section calculated based on tail heights for 3 keV He<sup>+</sup> scattering, according to Eq. (5). Labels indicating the target element are on the left side of each datapoint.



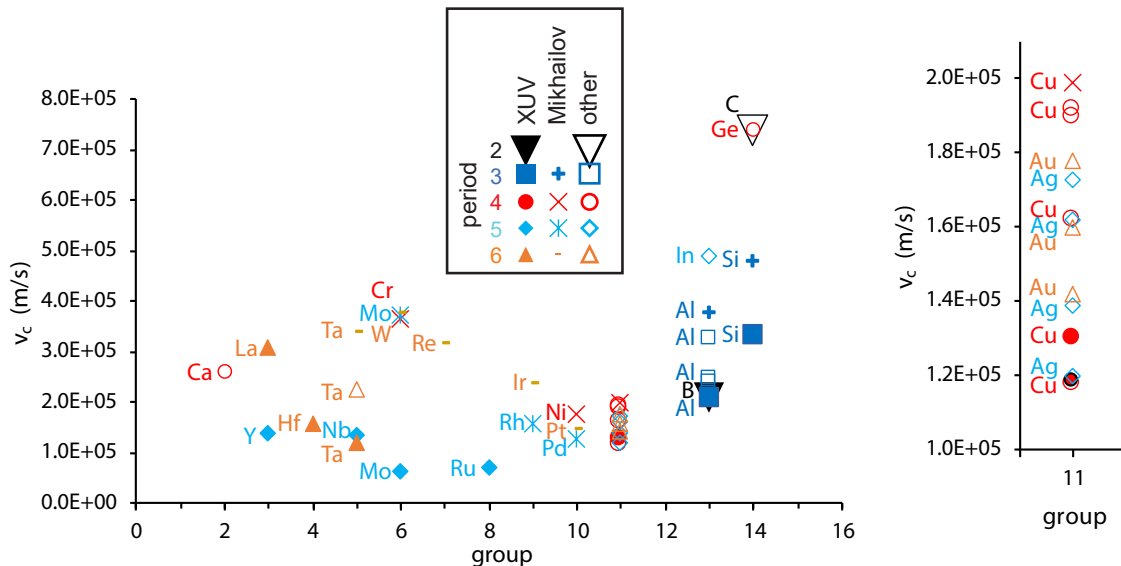
**Fig. 4.** Open symbols (left axis): estimated reionisation probability or ratio of signals for He<sup>0</sup> and He<sup>+</sup> scattering I<sup>0</sup>/I<sup>+</sup> after Souda et al. [15]. Filled symbols (right axis): reionisation cross-section  $\sigma_R$  from LEIS tail heights divided by the ion fraction P<sup>+</sup> based on characteristic velocity measurements. Element labels are on the left-hand side of data points. Various symbols and colours indicate different periods (rows) in the periodic table according to the legend.

be strongly influenced by the ion fraction of the He<sup>+</sup> scattering experiments they used as reference.

4.4. Comparison of reported characteristic velocity values

As last part of our comparison of charge exchange data from our laboratory with data reported in literature, we take a closer look at  $v_c$  values for He<sup>+</sup> neutralisation by solid targets, which are plotted in Fig. 5 and listed in Table 1. The first systematic investigation of  $v_c$  values for various elements was published by Mikhailov et al. [13]. It should be noted that these data were originally reported relative to the  $v_c$  value for Pd, these values have been converted to absolute values by reading the  $v_c$  value for Pd from the graph published in [13]. Other literature values are indicated by open symbols, while values measured in our laboratory are indicated by solid symbols.

Our data reproduces the qualitative trend found by Mikhailov et al.: for transition metals the  $v_c$  value initially decreases with increasing group number (increased filling of the d electrons bands), but rises again for Cu and the non-transition metal elements in group 13 and 14. Before discussing the deviations between the datasets from different sources, we discuss the largest outliers from the general trend. On the left side, the  $v_c$  value for La is much higher than for other metals studied in our laboratory. This may be caused by the low work function of La, which leads to efficient resonant neutralisation by conduction band electrons [21]. Additionally, La belongs to the lanthanides and may therefore fall out of the general trend of transition metals. On the other side of the periodic table, very high  $v_c$  values were reported for C (highly oriented pyrolytic graphite) and Ge. In the case of graphitic C, efficient resonant neutralisation is possible due a broad valence band that extends down to the He 1s level [20,23], while for Ge the ion yield was reported to be



**Fig. 5.** Characteristic velocity values for He<sup>+</sup> neutralisation on solid pure elemental targets. Element labels are on the left-hand side of data points. Various symbols and colours indicate different periods (rows) in the periodic table according to the legend. Solid symbols (column label XUV) correspond to data from our laboratory, symbols +, ×, \*, - are reproduced from Mikhailov et al. [13], open symbols (column label other) are values from other literature sources according to Table 1. The right part of the figure shows a magnification for group 11 elements. In this part the solid red circle corresponds to polycrystalline Cu foil and the solid red circle with black outline to a sputter deposited Cu film.

oscillating vs.  $1/v$ , which is indicative for quasi-resonant charge transfer [29]. Since resonant charge transfer processes are expected to have high rates compared to other mechanisms, it is reasonable to assume that this explains high  $v_c$  values compared to other elements.

Despite the similar global trend in  $v_c$  vs. group number for data from various sources, there exist large differences in absolute reported values for the same element. The values reported by Mikhailov et al. are in nearly all cases higher compared to data from other sources, while values from our group are consistently in the lower range of reported literature values. Likely origins for these differences include (i) instrumental effects and data analysis, (ii) influence of surface structure/morphology and (iii) influence of contamination. In order to assess the effect of instrumental effects and data analysis (i), we refer to reported results from a round robin interlaboratory study on pieces of Cu foil from the same batch, measured with 5 Qtac<sup>100</sup> instruments in different laboratories [39]. The  $v_c$  values for Cu from this study ranged from  $1.13 \times 10^5$  m/s to  $1.46 \times 10^5$  m/s according to evaluation of the operator of each instrument. When the raw measurement data from different instruments was evaluated by a single operator, this scatter reduced to a range from  $1.25 \times 10^5$  m/s to  $1.46 \times 10^5$  m/s. This shows that for the same type of instrument as used in this study, the  $v_c$  measurement for the same material can be reproduced with a much better accuracy compared to the typical scatter in data from different publications (Fig. 5). Unfortunately this round robin study did not include other types of LEIS instruments, such that a possible effect of instrument type remains unknown. Also it should be noted that for Cu there is little variation in peak area evaluation expected depending on the exact fitting procedure, since Cu spectra hardly show any LEIS tail. For elements with significant reionisation, a stronger influence of peak fitting procedure can be expected. Crystal structure and sample morphology (ii) may affect the ion fraction (and thus  $v_c$ ) because of variation in electron density along the ion trajectory [3]. For studies where  $v_c$  was determined both on polycrystalline and/or various single crystalline materials in the same scattering geometry and same publication, the absolute deviation between lowest and highest value was  $0.19 \times 10^5$  m/s for Ag [31],  $0.3 \times 10^5$  m/s for Al [32] and  $0.4 \times 10^5$  m/s for Cu [17]. This spread is in the same range as the instrument-to-instrument variation for different Qtac instruments in the Cu round robin study, so it is unlikely that structure or morphology alone can explain the large deviations between various datasets. As last possible source of deviations we discuss the potential influence of contamination (iii). In case of absence of matrix effects, i.e. the  $v_c$  value for neutralisation of He<sup>+</sup> on a specific element is independent of the chemical surrounding of the element, no effect of contamination on the  $v_c$  value would be expected. However, previous studies showed that oxidation of transition metals does result in matrix effects of the ion fraction for He<sup>+</sup> scattering on metal atoms in metal oxides [19,22]. The  $v_c$  value for scattering on metal atoms in stoichiometric metal oxides can be up to a factor 4 higher compared to sputter cleaned metals [22]. It may thus be that a small coverage of oxygen or carbon contamination significantly influences the  $v_c$  value. Since the sensitivity of LEIS for low  $Z$  elements is much smaller compared to the sensitivity for heavier elements, it may be that a small contamination that is not visible as C or O surface peak, still does influence the measured  $v_c$  value. The measurements in our laboratory were all carried out directly after sputter cleaning of the sample. Most other literature values for  $v_c$  were obtained from samples prepared by sputtering and annealing. The annealing step implies longer exposure of the sample to residual gases in the vacuum system, which may lead to surface contamination.

## 5. Discussion

This systematic investigation of LEIS tails and surface peaks for He<sup>+</sup> scattering on various target elements confirms some of the findings on charge exchange properties in previous systematic studies by Aono and Souda et al. [3,15] and Mikhailov et al. [13], while it indicates that the absolute strength of reionisation in the few keV LEIS regime is not

properly predicted by the reionisation probability previously estimated by Souda et al. In this section we discuss the physical mechanisms behind our findings.

As discussed in the introduction, reionisation of neutral He by a solid target is possible through resonant charge transfer (when energy levels of the target and He have closely matching electron energy) or by charge transfer in close collision, when He and a target atom may form a quasi-molecular state. Resonant charge transfer can be experimentally observed as an oscillating ion yield vs. reciprocal velocity. For the target elements in this study that were measured in our laboratory, significant oscillations were only observed for La [21]. Thus, it can be assumed that for all other elements, reionisation (if observed) should occur due to charge transfer in close collision. In line with previous results reported in literature for reionisation of He<sup>0</sup> in backscattering experiments and reionisation observed through LEIS tails, our results confirm that for transition metals, the energy threshold for reionisation increases with increased filling of the d electron band (increasing group number in the periodic table). Aono and Souda formulated the hypothesis that for elements with a higher filling of the d electron band, a closer approach between He and target atom is needed for formation of a quasi-molecular state that is required for reionisation to occur [3]. This closer approach is reflected in a higher reionisation threshold, since the distance of closest approach in a scattering event is smaller for higher primary energy [1].

Next, we discuss the trend in characteristic velocity versus group number (Fig. 5). Data from Mikhailov et al. and our laboratory indicate that for transition metals,  $v_c$  values show a decreasing trend (meaning less strong neutralisation) for increasing number of d electrons up to around group number 10. Before discussing this trend in terms of charge transfer in close collision, as we previously did for the reionisation threshold, we should consider the main mechanism of charge transfer. It should be noted that for all elements in group 11 and 12, as well as for a significant number of elements in group 10, the reionisation threshold was reported to be  $>2$  keV, which indicates that charge transfer in close collision is impossible or less likely. Since none of these elements has resonant energy levels with He, this implies that Auger neutralisation should be the dominating charge exchange process for targets with higher reionisation threshold. For Cu, inverse velocity plots from literature and our work show that the measured surface peak signal divided by scattering cross-section (proportional to ion fraction) starts deviating from the fitted  $v_c$  value for a primary energy  $>2.2$  keV, which is attributed to the influence of collision induced charge exchange processes on the final ion fraction. For this reason, the fit of  $v_c$  reported in this work (and other references), was determined for primary energies up to 2.2 keV and thus only reflects the ion fraction due to Auger charge transfer. On the contrary, the reionisation thresholds for transition metals from group 3 to 9 considered in this overview are all  $<1$  keV, while the  $v_c$  was determined for primary energies in a range from 1 to 3.5 keV for the data by Mikhailov et al. or from 1 keV up to around 4–5 keV for the data from our lab. This implies that for elements from group 3–9, charge transfer (neutralisation and reionisation) in close collision is active in the entire energy range used for the determination of  $v_c$ . Since it is generally stated that charge transfer in close collision is more efficient (i.e. has a higher rate) than Auger charge transfer for the same ion/target combination, we assume that for transition metals from group 3–9, as well as for other elements with a reionisation threshold below about 1 keV, charge transfer in close collision is the dominating mechanism and hence determines the  $v_c$  value. The only exception are elements for which resonant charge transfer is observed: for those elements resonant charge transfer may dominate the  $v_c$  value.

For the transition metals from group 3–9, for which charge transfer in close collision is the dominating charge exchange mechanism, the characteristic velocity decreases with increased filling of the d bands. In order to explain the dependence of reionisation threshold on d band filling, Aono and Souda formulated the hypothesis that for elements with a higher filling of the d band, a closer approach of the He atom is



needed for charge transfer in close collision [3]. Along the same line, we can formulate the hypothesis that a smaller distance of closest approach needed for charge transfer in close collision, implies a lower average rate of charge transfer along the trajectory of a backscattered  $\text{He}^+$  ion. Since neutralisation (and not reionisation) is thought to be the dominating charge transfer process for  $\text{He}^+$  backscattering events that lead to a surface peak, a lower charge transfer rate implies less efficient neutralisation and thus a lower  $v_c$  value.

Now we have seen that the reionisation threshold and neutralisation efficiency ( $\text{He}^+$  backscattering  $v_c$  value or ion fraction) scale with d band filling for those transition metals for which charge transfer in close collision is dominating, the question arises why no such trend can be discovered in the reionisation cross-section based on 3 keV  $\text{He}^+$  LEIS tails, as reported in Fig. 3. The LEIS tail is formed by neutralised He atoms that backscatter on sub-surface atoms and reionise by interaction with a surface atom in close collision, before they leave the target. It is thus logical to assume that the reionisation step in close collision is the dominating charge exchange process that determines the final ion fraction. One would thus expect that an increased filling of the d band implies a lower average charge transfer rate (as argued before) and thus a lower reionisation cross-section. We propose that such a dependence is not observed in our data, because we determine the reionisation cross-section at an ion energy far above the reionisation threshold, which is  $< 0.9$  keV for all elements for which we observed a significant LEIS tail (all investigated elements except Cu and Au). The final ion fraction of sub-surface scattered He neutrals is determined by various factors that have partly distinct velocity or energy dependence. A higher energy implies that the  $\text{He}^0$  particle approaches closer to the target surface atom causing reionisation. Since reionisation only happens in close collision, with larger energy also a larger fraction of the trajectory of the ion along this surface atom contributes to reionisation. It can thus be expected that, for energies just above the reionisation threshold, a higher energy leads to a higher ion fraction. On the other hand, higher energy (velocity) implies that the He particle spends less time close to the surface atom, which eventually reduces the probability for reionisation, since the charge transfer rate has a finite value. Lastly, the energy also still influences the probability that a reionised He atom survives Auger neutralisation on the outgoing trajectory towards the detector, which leads to an increasing ion fraction for larger energy. It is thus reasonable to assume that the fraction of reionised He neutrals saturates with increasing energy far enough above the reionisation threshold, although a proof of this would require a more solid theoretical understanding of the involved charge transfer rates, which is currently not available. As support for the assumption that the reionisation probability saturates with increasing energy, we note that Brüner et al. investigated the energy dependence of the reionisation probability for  $\text{He}^+$  scattering an  $\text{Al}_2\text{O}_3$  target by comparing LEIS tail measurements from a wide range of primary and final energies with TRBS simulations [27]. These results indeed point at a saturating behaviour of the reionisation versus energy for an  $\text{Al}_2\text{O}_3$  target, such that it is reasonable to assume that this may also be the case for other elements. Saturation of the reionisation may also be an additional reason why we do not observe a systematic dependence of the reionisation cross-section on electronic structure of the target (for 3 keV  $\text{He}^+$  LEIS tails), contrary to the previously published estimate of the reionisation probability of 1 keV  $\text{He}^0$  by Souda et al. [15].

Finally, we discuss the main limitations of the approach described in this work. The main limitation for determining reionisation from the tail height, is the use of a single primary energy. In order to reduce the influence of the exact multiple scattering trajectories on the reionisation strength extracted from the tail intensity as much as possible, we only considered the tail intensity just below the onset of the surface peak. Since the energy of the surface peak varies with target atomic mass according to the kinematic factor, this means that the reionisation strength for He interacting with different elements is not compared for exactly the same He energy. Since systematic trends in charge exchange

with electronic structure were mainly considered for transition metals, we estimate the uncertainty of this approach by comparing the kinematic factor for Y and W, the lightest and heaviest transition metals for which we observed a tail. These kinematic factors are 0.85 and 0.92, respectively, and thus differ by about 8%. This makes it extremely unlikely that differences in final energy at which the tail signal is evaluated, influence the outcome of the derived reionisation cross-section for elements from the transition metals. In addition, it should be noted that there appears no correlation between the reionisation cross-section and target atomic mass (see results in Fig. 3), which supports the assumption that the influence of final energy is minor. As mentioned in the introduction, a more rigorous way to take multiple scattering into account, would be the use of TRBS simulations, which would allow to calculate the reionisation function as a function of final energy. However, this approach is considered beyond the scope of this work, since not for all elements reliable values of the electronic stopping correction factor are known.

For the systematic comparison of neutralisation of backscattered  $\text{He}^+$  ions, i.e. the  $v_c$  values in Fig. 5, the main unanswered question is the large deviation in absolute values of the  $v_c$  reported by different laboratories for the same target element. The main difference in sample preparation between our work and that of Mikhailov et al. and most other references, is that we studied sputter cleaned samples, while Mikhailov et al. studied sputtered and annealed targets. Annealed surfaces are smoother on the atomic length scale, which may result in a different electron density profile at the surface and therefore different charge exchange rates. Unfortunately the sample holder of our LEIS instrument is not suitable for sample preparation by annealing under good vacuum conditions for preserving a clean metal/elemental surface. Therefore this potential difference between sputtered and sputter-annealed surfaces cannot be investigated in our laboratory. However, the comparatively small differences in  $v_c$  between different crystal orientations of the same target reported by the Bauer group (see Section 4.4 and [17,31,32]), make it unlikely that surface structure can explain the difference between our data and the data of Mikhailov et al. This leaves us with two remaining hypotheses, that the difference is either caused by a small surface contamination that does not result in a visible LEIS signal, or by a systematic difference in data acquisition and analysis.

## 6. Summary and conclusions

In summary, we presented a systematic comparison of the reionisation and neutralisation of  $\text{He}^+$  ions by a large set of solid pure elemental targets, by comparing the surface peak and tail signals of LEIS spectra. Our results confirm the previously described trend that the reionisation threshold for scattering on transition metals systematically increases with increased filling of the d electron bands. However the magnitude of the reionisation probability of 3 keV primary energy  $\text{He}^+$  ions, as extracted from the tail height of LEIS spectra, shows no systematic trend with electronic structure as previously derived for the reionisation of 1 keV He neutrals in a backscattering geometry. Our analysis revealed that the trend in the latter case must have been strongly influenced by the ion scattering yields used as reference in those experiments. In addition, a possible saturation of reionisation probability with increasing energy may contribute to the absence of any trend in our reionisation values. Our systematic analysis of characteristic velocity values for neutralisation of  $\text{He}^+$  in backscattering experiments confirms the ‘v shape’ curve originally presented by Mikhailov et al., where the characteristic velocity decreases with increasing group number in the periodic table, but rises again for elements in the Cu group and steeply increases for non-transition metals on the right side of the periodic table. The systematic dependences of reionisation threshold and neutralisation probability were discussed in terms of influence of d band filling on charge exchange in close collision. Interestingly, we note that the characteristic velocity value of  $\text{He}^+$  on Cu, measured in an energy range where Auger neutralisation dominates the ion fraction, is similar or higher than the

characteristic velocity values measured for transition metals where charge exchange in close collision is contributing to the ion fraction. Previous reviews suggested that neutralisation in close collision in general has a higher charge exchange rate than Auger neutralisation [2]. Our measurements indicate that the charge exchange rates of both processes can be similar. The relative strength of neutralisation thus cannot be simply estimated based on the dominating charge transfer process, but has to be measured whenever detailed knowledge of charge exchange is required.

This work provides important background knowledge for the quantitative interpretation of LEIS surface peaks and tails. Even though the product of scattering cross-section and ion fraction can be considered as a sensitivity factor for LEIS surface peaks (analogous to for instance sensitivity factors for electron spectroscopy techniques), the large scatter in reported absolute values of the characteristic velocity for neutralisation from different sources and different surface structure shows that deriving generally valid sensitivity factors for LEIS may be elusive. It is thus important to perform quantification based on reference samples, or determine the strength of neutralisation and reionisation with reference samples.

### CRedit authorship contribution statement

**J.M. Sturm:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Supervision, Funding acquisition. **H.W. Lokhorst:** Investigation, Formal analysis, Writing – review & editing. **A.A. Zameshin:** Conceptualization, Methodology, Investigation. **M.D. Ackermann:** Writing – review & editing, Project administration, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request, depending on clearance from industrial partners.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nimb.2023.02.029>.

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