Six decades of atomic collisions in solids

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Published in:
Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms

DOI:
10.1016/j.nimb.2016.12.004

Publication date:
2017

Document version
Early version, also known as pre-print

Citation for published version (APA):
Abstract

In response to an invitation by the organizers of the 27th international conference on atomic collisions in solids, a brief survey is presented, starting from the roots of the field in the 1950s and 1960s, of some major discoveries, longstanding problems, surprising findings and memorable controversies in topics covered by the conference. Considering the breadth of the field, the selection of topics is necessarily subjective, but with the emphasis on channeling, stopping and sputtering, three topical areas are discussed which have been active from the early 1960s until now.

Keywords: Atomic collisions, Channeling, Stopping power, Sputtering, Charge states

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1. Introduction

Atomic Collisions in Solids, also known as particle-solid interaction, is the common term for a branch of accelerator-based physics with a wide range of applications in science and technology. The roots of the field date back to the middle of the 19th century with the study of phenomena in gas discharges. Early in the 20th century, after the discovery of radioactivity, exploration of the penetration of charged particles in matter and their accompanying ionization phenomena became an active research area. During the first half of the 20th century it was not the least theoretical studies of atomic-collision processes which paved the way for the development after World War II.

Figure 1 shows publication activity from 1945 until now in three major topical areas, radiation damage, stopping and sputtering\(^1\).

The overall behavior is exponential over several decades, but there are significant differences between the three chosen fields. Radiation damage shows a very steep rise after 1950 and a more moderate slope from 1970 on. Sputtering shows a similar behavior, although the expansion rate is significantly higher than that of radiation damage from around 1975, with a publication rate of \(\approx 5000\) papers per year in 2015. Note, however, that both sets of data include activities that may be far from fundamental research in collision physics. A different behavior is seen in the field of stopping, where we see a constant activity level until \(\approx 1965\), the time of the first ICACS conference, a rapid rise until 1990, and a constant level at \(\approx 150\) publications per year ever since.

A few distinct events in the 1950s have contributed to mark a new era in collision physics.

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\(^1\)This graph is supposed to show qualitative trends, considering both the choice of keywords and well-known weaknesses of the Web of Science [1]
As a consequence of US president Eisenhower’s legendary ‘Atoms for Peace’ speech in 1953, an international conference on peaceful use of atomic energy was called to Geneva in August 1955 [2]. It was in this period that wartime research in nuclear science and technology was declassified, opening up for an abundance of activities, in particular research in isotope separation and radiation damage. Isotope separators, nowadays called ion implanters, became the leading tool for research in atomic collisions in solids for several decades to come. Radiation damage has been an active area ever since.

Also in 1955, Gottfried Wehner published his famous paper on sputtering of metal single crystals by ion bombardment [3] (Fig. 2). That work had a seemingly narrower scope, yet from the point of view of the topical area discussed here it was central: Controlled collision experiments with single crystals were a new feature and became a central activity ever since. Moreover, after about half a century of discussion about whether phenomena like ion-electron emission and sputtering had to be understood in terms of momentum transfer in atomic collisions or as local evaporation, ‘Wehner spots’ reflecting the crystal structure in the angular emission pattern of sputtered atoms were instantaneously taken as evidence supporting the dominating role of atomic collisions in the process. More on this point in Sect. 7.1.

Already in 1951, N. O. Lassen [4] had reported measurements of the charges of fission fragments penetrating through matter, where he found significantly higher charges for penetration in solid than in gaseous targets (Fig. 3). These measurements marked the starting
point of a new field of research, atomic physics with swift heavy ions, and their interpretation gave rise to a long-lasting controversy from the 1970s to the end of the past century. More on this point in Sect. 6.5.1.

- The last item to be mentioned here is Lindhard’s [5] dielectric theory, which is an expansion of classical Drude-Lorentz electrodynamics of material media. Lindhard theory is based on quantum instead of classical mechanics and allows for rapidly varying electric and magnetic fields via a dielectric function $\epsilon(k, \omega)$ which depends on both frequency and wave number. This has proven to be a powerful and versatile formalism and acknowledged as a useful
tool in many-body electron theory because of its conceptual simplicity. The original paper [5] offered applications both in condensed-matter physics and in particle penetration. The theory was exemplified on the Fermi gas, and its combination with the Thomas-Fermi principle, or local density approximation, provided a badly-needed tool for semi-quantitative calculations of energy losses in condensed matter for several decades.

In this report I have chosen to illustrate the development of the field of atomic collisions in solids on three topical areas, channeling, stopping and sputtering, which have been amongst the prime issues at all ICACS conferences over half a century. I have tried to focus on landmarks where either longstanding problems were solved or new activities opened. Considering the amount of acquired knowledge indicated by figure 1, I kindly ask the reader to bear over with the fact that both the choice of topical areas and selected landmarks to some degree reflects my own experience in the field, and the degree of detail reflects to some extent the time periods of my engagement.

2. Drivers of the Development

The field of atomic collisions in solids is characterized by tight interaction between theory and experiment, as well as between basic and applied research.

Radiation damage in materials, particularly in graphite, had been identified as a prime topic to be concerned about in the construction of the first reactor during the Manhattan project in World War II. A report by Seitz [6] stimulated a wealth of experimental and theoretical studies, not only of radiation damage in numerous materials but, just as important, of a wider range of collision phenomena.

Another major driving force came from nuclear physics. In 1955, leading groups in isotope separation gathered at Harwell [7], discussing ion sources, target preparation and collection problems. By 1965, the time of the first ICACS conference [8], ion sources and target preparation had been studied widely and successfully, while collection problems, addressing the concentration of foreign atoms that could be incorporated into a material by implantation, needed fundamental knowledge of ion penetration, sputtering and radiation-enhanced diffusion which was still nonexistent.

The development of integrated microelectronic circuits has been a major driving force for basic research in collision physics from the mid 1960s, as documented already in the proceedings of ICACS-1 [8]. It was particularly developers of particle detectors who had the right mix of expertise in solid-state and accelerator physics to lead this development [9].

Numerous applications of atomic-collision phenomena in solids showed up in the following years. Materials science has been one of the main objects, in particular ion beam analysis by a variety of accelerator-based techniques, ion-beam modification of all kinds of materials, as well as basic research in diffusion phenomena. Ion-beam modification became the topic of a separate conference already in 1970, and ion-beam analysis followed in 1973.

An example of the opposite order of events is the discovery of organic mass spectrometry by particle bombardment, also called PDMS (plasma desorption mass spectrometry), by nuclear physicists [10] and subsequently discussed vividly in the atomic collisions in solids community for several years. Interest in that area decreased temporarily with the emergence of laser-based technologies but come up again more recently under the name ‘MeV-SIMS’.

A particular feature is the phenomenon of sputtering which, during the 1960s, became more or less split between two topical areas, sputter emission or erosion on the one hand and sputter
deposition on the other. Sputter emission is genuine atomic-collision physics and central to applications in basic and applied surface physics and chemistry. Sputter deposition is an important tool in thin-film technology. Research in sputter emission accounts for most activities in sputtering indicated in figure 1 until around 1975, while sputter deposition took over gradually and has been dominating from the late 1980s.

3. Experimental Tools

Numerous experimental tools, developed in other branches of science and technology such as ultrahigh vacuum, particle accelerators and detectors as well as sample preparation, especially crystal growth, have become necessary ingredients in atomic-collision physics. In other areas such as structure analysis, electronics and computers there was also substantial feedback in the opposite direction.

Several types of particle accelerators were developed initially for protons, alpha particles or electrons. Experiments involving other ions required special ion sources. The major challenge in experimental research on atomic collisions was the development of ion sources enabling acceleration of an arbitrary isotope of an arbitrary element up to a well defined energy. That development took place from the mid 1950s over most of the 1960s. The energy range available for acceleration of heavy ions increased gradually from $\sim 100$ keV in 1960 to the TeV regime at the turn of the century.

Beams of molecular ions had been employed early on, mostly with the aim of decreasing the beam velocity for a given acceleration voltage, but from the early 1970s molecular beams were used to investigate new physics [11, 12].

Antiprotons, discovered in 1955, result from nuclear reactions at high-energy accelerators. Hence, instead of an accelerator a source of antiprotons for atomic-collision studies is typically a decelerator. While the prime motivation for building such facilities is the study of antimatter, limited access has been provided from the late 1980s to atomic-collision experiments with both gas and solid targets [13].

4. Theoretical Aspects

Here I wish to mention two features in the development that are common to all topical areas in consideration.

4.1. Elastic versus Inelastic Collisions

When going through the literature you will notice a trend in the field of atomic collisions in solids from nuclear (elastic) towards electronic (inelastic) collisions. Collisions between heavy particles tend to be more or less elastic at low energies where there is not enough energy to cause ionization or excitation. Conversely, collisions at high energy were found to be inelastic already in the first cloud-chamber photographs of a radioactive decay: MeV alpha particles are rarely deflected while vividly ionizing the penetrated medium.

For a long time there was uncertainty regarding the transition between the two regimes. In the early radiation-damage literature you will find the claim that collisions are elastic up to a projectile energy $\sim 1$ keV/u. This appears to be a simplified version of a relation by Seitz [6], based on the energy transferred from a heavy particle to an electron at rest. According to Bohr’s adiabaticity criterion the transition would be found at approximately the Bohr speed, i.e., at an
energy $E \sim 25$ keV/u. Both estimates ignore the orbital motion of target electrons which, for a free electron gas, was found to lead to velocity-proportional electronic energy loss by Fermi & Teller [14].

All these estimates became obsolete with the appearance of the LSS theory [15, 16] – more on this in Sect. 6.2 – which predicted a rather broad transition regime between predominantly nuclear and predominantly electronic stopping. Nevertheless, the assumption of elastic scattering in all early theory of radiation damage and sputtering appears well justified at beam energies in the lower to median keV range. A more serious simplification is the assumption of hard-sphere (billard ball) scattering, which you find in most of the literature in the pre-LSS era.

4.2. Classical versus Quantum Mechanics

According to Bohr [17], classical scattering theory and Born approximation are complementary in the sense that an overlap in the range of validity of these two descriptions of collision processes exists but is rather narrow. The Bohr criterion sets an upper limit of classical scattering theory via the relation

$$\kappa = \frac{2v_0e_1e_2}{e^2v} > 1,$$

where $e_1$ and $e_2$ denote the charges of the collision partners, $v$ their relative speed, and $v_0$ the Bohr speed. For collisions between heavy particles this implies that the classical limit, expressed in relative energy, becomes proportional to the reduced mass as well as the square of the nuclear charge numbers. For ion-electron collisions, on the other hand, Eq. 1 reduces to $E < Z_1^2 \times 0.1$ MeV/u in terms of the ion energy.

Consequently, collisions between heavy particles obey classical scattering up to very high ion energies, while electronic processes may have to be treated quantally for a wide range of particle types and energies. Computer codes to simulate collisions in solids describe the motion of projectile and target nuclei in terms of classical equations of motion. To the extent that electronic processes need to be involved, this is usually achieved by input quantities such as stopping cross sections and ionization rates or, more rarely, by explicit quantum molecular dynamics.

5. Collisions in Crystals. Channeling

5.1. Emission Phenomena

Wehner’s experiments on emission patterns in single-crystal sputtering (Fig. 2) inspired other groups to study collision phenomena involving crystals. In 1959, Rol et al. [19] showed that the sputter yield, i.e., the total flux of emitted atoms per incoming ion, did not only depend on the angle of incidence but also on the crystal orientation. Figure 4 shows an example from subsequent work by Almén & Bruce [18].

A qualitative explanation of this effect was offered in refs. [23, 24], which involved a crystal model made up by hard spheres. If such a crystal is oriented along some close-packed direction like [100], it looks transparent. It was argued that a projectile impinging near such a direction would penetrate deeper before undergoing a collision than when coming in a random direction. Within the reasonable assumption that the sputter flux caused by a recoiling atom would decrease with increasing depth of its origin, it follows that ions hitting a surface parallel to an open lattice direction would lead to a local minimum in the sputter yield. Similar effects were reported from measurements of ion-induced electron emission from single crystals [25, 26].
Since saturation and sputtering are related, we have ... a greater difference. Probably either the oxide layer on Al, or the higher Kr concentration in Al compared with Ce throughout the series of experiments, although crystalline Cu also is given for different angles of incidence. The single crystal retained its appearance, and also that the damaged layer is continuously sputtered off. From a comparison of figs. 27 and 28 we see that saturation and sputtering are related, since the intervals between the measuring points are too large. It is also to be noticed that the penetration depth cannot be proportional to the saturation value. However, the measurements indicate that also in a crystalline material is nearly constant. In the same way there is a constant ratio between the minima of saturation in the single crystal and of the sputtering of polycrystalline material.

While early theoretical descriptions of these phenomena [23, 24, 27] involved adjustable parameters, more recent calculations by binary-collision [28] or molecular-dynamics [29] codes predict the main features directly with an error margin given by the adopted interatomic potential.

5.2. Ion Ranges and Stopping

Another kind of anisotropy was discovered in the energy loss of ions. From 1956, Davies and colleagues at Chalk River in Canada developed a novel technique to measure heavy-ion ranges in solids. Ion ranges had been measured previously with fission fragments at MeV energies [4], but nuclear physicists at Chalk River needed ranges in the keV energy range in order to determine energies of atoms recoiling from nuclear reactions. Such ranges may be in the nanometer range. The new technique, involving implantation of radioactive ions and subsequent etching by anodic oxidation [30], was a milestone in atomic-collision physics and an archetype of depth profiling, a process indispensable in all development of micro- and nano-electronical devices as well as surface science and technology.

Distributions in the penetration depth of ions such as alpha ranges had long been known to be close to gaussian. Measurements by Davies et al. [20] showed pronounced exponential tails over a wide range of beam energies (Figure 5). Attempts were made to rationalize the origin of these
tails, but a convincing explanation came from a different community: In Oak Ridge, a group of theoreticians under D. K. Holmes studied collision cascades initiated by atoms in the keV energy range with a view to recoil atoms from collisions with fast neutrons. In order to test predictions by transport theory for random media, calculations were performed numerically assuming binary collisions in a crystalline medium. As could be expected, atoms moving along an open direction, a 'channel', penetrated more deeply than average.

The suggestion came up that exponential tails, found at Chalk River for polycrystalline targets, originated in ions penetrating deeply in crystallites aligned to the incident-beam direction. Measurements in a single crystal confirmed this suggestion (figure 6), and good qualitative agreement was obtained with simulations (figure 7), albeit with different ion-target combinations and beam energies.

5.3. Guided Motion

In the qualitative explanation of the anisotropy phenomena discussed above one may assume particles to move along straight lines until the first violent collision. This assumption entered explicitly the first theoretical treatment of channeling by Lehmann and Leibfried [35].

Figure 5: Integral distribution of penetration depth, i.e. the fraction of ions remaining in the target after layer-by-layer etching for Cs\(^{137}\) ions in aluminium. Lines to guide the eye. From [20].
However, this picture was found unlikely to explain measurements by Dearnaley [36] which showed average energy losses of MeV proton beams in gold to be significantly lower in certain directions than in a polycrystal. MeV protons have penetration depths in the micrometer range, where multiple scattering would give rise to deviations from straight lines by far more than the width of a channel.

In 1964, Lindhard [37] proposed that trajectories of particles in closely-packed directions were guided, and the basic process was asserted to be scattering on a string rather than on a single atom. As indicated in figure 8, for a small angle of incidence on such a string, the repulsive forces exerted by the string atoms gently reflect the incident ion. The trajectory will in general not be planar. If, as a first approximation, energy loss is neglected, the angular momentum around the string will be conserved.

Within this framework,

- There is a critical angle within which a projectile is reflected from a string,
- Close collisions with individual atoms must be suppressed, and
- Trajectories are generally not confined to channels. Therefore, Lindhard spoke of guided rather than channeled motion.

In this picture, guided motion affects energy loss, multiple scattering and related phenomena, but these features are secondary compared to effects related to the suppression of close collisions,
These "channeled" particles did not experience very many glancing collisions with atoms of the lattice, which steered them into preferred channels. In each case, the preferred channel for particles incident upon (111) from about 3 keV. In this prediction, the ability of channeling remains roughly constant at 1%.

The Born-Mayer potential of Gibson and others was chosen as more realistic than the Bohr potential calculations for particles normally incident upon (100). The half-thickness of the experimental tails is prohibitively small for particles incident upon (110). This division is also evident from Fig. 1. The small penetration portion of the curves in Fig. 1 are modal. The small penetration portion consists of the channeled particles and their initial direction of motion.

The initial force on a charged particle is in the direction of the electric field and is deflected in the static Cu lattice. The particle's direction is changed by the electric field. Preliminary calculations for diamond and bcc Cu atoms normally incident upon the crystal surface. In the isotropic case, the force on the particle is not restricted to fcc crystals. Recent work on high energy sputtering ejection parameters of the curves in Fig. 8 shows the small penetration portion of the curves in Fig. 1 are modal. The small penetration portion consists of the channeled particles and their initial direction of motion.

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in the \((p, \gamma)\) reaction yield around a closely-packed crystal direction, and a compensating shoulder in the transition region toward the result for random incidence. Subsequent measurements by many groups confirmed the validity of Lindhard’s prediction of much more pronounced dips for numerous ion-target combinations, not only on nuclear reactions (cf. Fig. 13).

An unusual feature of Lindhard’s paper [37] is the complete absence of any literature references. While one may discuss whether this was fair towards those who had paved the way, one may argue that the theory does not build on related previous work other than elementary textbook physics.

A full subsequent paper [31], one of the highlights in the field of atomic collisions in solids, made up for this and, in addition to quantitative estimates of a number of secondary effects, presented two additional results of primary importance,

- The fact that guided trajectories avoid close collisions implies that particles emerging from regular lattice sites, e.g. from radioactive decay or after Rutherford scattering, will not undergo guided motion. This effect, later called blocking [38], was demonstrated by Domeij and Björqvist [33] and is illustrated in figure 10.

- In addition to string scattering, now called axial channeling, closely packed lattice planes
may likewise affect trajectories in the way sketched in figure 8. Here, trajectories are confined between neighboring lattice planes, as proposed by Erginsoy et al. [39]. A convincing demonstration of this was presented by Tulinov [34], shown in figure 11, which is actually a blocking pattern generated by protons incident on a tungsten crystal along a random direction. Planar blocking is the origin of numerous straight lines in the figure.

It may be appropriate to mention that figure 11 shows the result of Rutherford’s original scattering experiment performed on a crystal instead of a gas or a polycrystal. One may ponder about how much time it would have taken to formulate Rutherford’s law, if all early experiments had been performed on a crystal rather than foils or gas targets.

Lindhard’s paper stimulated numerous activities in both experiment and theory for several decades, not the least simulational studies. This includes the effect of thermal motion of the lattice atoms, multiple scattering and energy loss of the projectiles, transition between guided and random motion (dechanneling) and, in particular, numerous applications such as lattice location of implanted ions, depth profiles of defects and impurities, lifetimes of nuclear reactions and others. More recently, Assmann et al. [40] found a gradual transition from channeling to blocking behavior for ions from C to Au in the transmission through a [100] direction of a Si crystal. The phenomenon was found to be related to capture and loss of electrons by the penetrating ions which causes energy loss and, hence, deviations from reversibility of guided motion. For a recent review I refer to a summary by J. U. Andersen [41] which was reprinted in Ref. [42].

I conclude this section by a brief discussion of the role of quantum mechanics in channeling. Classical scattering theory breaks down at small scattering angles for an MeV proton in the
Figure 5: Angular distribution of protons elastically scattered from a tungsten single crystal at $E_u = 200$ keV. The photoplate was placed perpendicular to the [100] axis.

Figure 6: The solid lines are the intersections of the crystallographic planes with the plane which is perpendicular to the [100] axis. The numbers are indices of the crystallographic axes.

Crystallographic axes and planes, respectively, with the plane of the emulsion. Some of the axes are indicated schematically in fig. 6. The details of the experimental method will be published elsewhere [5].

Apparently, this photographic method is a straightforward and promising way of investigating complex crystal structures.


The orientation dependence of the emission of positrons and electrons from $^{64}$Cu embedded in single crystals has been investigated, showing a pronounced dip and peak in yield, respectively, in the axis direction.

During the last two years, different aspects of the Lindhard theory [1] of directional effects in the motion of fast charged particles in crystals have been investigated experimentally [2-5]. The present letter reports preliminary results of the emission from a copper single crystal of positrons and electrons from $^{64}$Cu atoms embedded in the crystal. The angular distribution of electrons emerging from a single crystal was already measured by Domeij et al. [3].

The orientation of the (100) axis of a copper single crystal cut along the {100} face was determined by the Rutherford scattering technique as described elsewhere [5]. By means of the isotope separator in Aarhus, an amount of $5 \times 10^{12}$ $^{64}$Cu atoms/cm$^2$ was injected into the crystal approximately along the (100) axis. Due to contamination from neighbouring isotopes, the total dose was $10^{15}$ Cu atoms/cm$^2$. The energy of the $^{64}$Cu atoms was 60 keV, and the penetration depth probably somewhat larger than ~200, which is the range in a "random" direction. $^{64}$Cu emits positrons as well as electrons, the maximum energy being 660 keV for positrons and 550 keV for electrons.

The experimental set-up consists of a goniometer, and a slit system which gives an angular resolution of 0.5 °. A magnet splits the beam into a/3+- and a/3-- component, which are counted simultaneously in two solid state detectors.

If we assume the $^{64}$Cu atoms to end up in lattice positions, the $^{64}$Cu-particles are emitted from the centers of atomic strings, and therefore their motion is expected to be steered by the rows of atoms as observed for a-particles by Domeij [2]. According to the Lindhard theory, it would be expected that the yield of positrons and electrons show a dip and a peak, respectively, near a major direction, e.g. the (100) axis.

In fig. 1 is shown the yield of emitted positrons and electrons as a function of the angle between the direction of emission and the (100) axis. The yield is normalized to the average yield in a

Figure 12: Emission of 150-250 keV electrons and 200-300 keV positrons from radioactive Cu$^{64}$ atoms injected into a Cu single crystal. From [43].

similar channeling dips, although with significant differences in the shoulders, and the graph on the right indicates oscillations in a quantal calculation involving 13 beams.

In addition to a channeling peak, another interesting feature in electron channeling is the formation of bound states. Bound states of electrons in the force field of a string must show analogies to those of bound states in the field of an atom. Transitions between these states must show up as channeling radiation, as predicted by Kumakhov [46] and verified experimentally subsequently [47].

Much of the development in the understanding of channeling phenomena after Lindhard’s pio-
neering work was based on computer simulations and, of course, experiment. After all, the 1960s also mark the beginning of the discipline of computational physics. Powerful simulation codes, starting with [48], brought much refinement and quantification. However Kumakhov’s prediction of channeling radiation, another landmark in the field, was the result of physical reasoning and standard tools of theoretical physics.

6. Stopping

Unlike channeling, which developed from scratch in the early 1960s, energy loss of charged particles was a well-developed field at that time, thanks to pioneering work by Niels Bohr, Bethe, Möller, Bloch, Lindhard and many others, as summarized in a classic of the field, Fano’s review from 1963 [49]. Why, then, did activity in the field rise from the mid 1960s at roughly the same rate as radiation damage and sputtering, as shown in figure 1?

Well, stopping theory was initially motivated by studies of the ranges of high-energy alpha and beta particles in matter. The standard of reference is Bethe’s well-known formula for the stopping force which reads, in its relativistic version,

\[
\frac{-dE}{dx} = \frac{4\pi Z_1^2 Z_2 e^4}{mv^2} NL
\]

with

\[
L = \ln \frac{2mv^2}{I} - \ln \left(1 - \frac{v^2}{c^2}\right) - \frac{v^2}{c^2}
\]

Figure 13: Channeling dip of 1 MeV positrons. Left: Comparison with 1 MeV proton bombardment for axial channeling around a (110) axis of gold. Right: Comparison of (111) planar dip calculated by multiple-beam diffraction theory (13 beams) with classical result, with and without thermal vibrations included. From [44].
where $Z_1$ and $Z_2$ are the atomic numbers of the projectile and target, respectively, $v$ the projectile speed, $c$ the speed of light, $N$ the number of target atoms per volume and $I$ a material constant defined as a logarithmically averaged excitation energy.

This formula gained importance in elementary-particle physics, and it was useful in all work involving swift protons when cyclotrons and van de Graaf accelerators became available. However,

1. Bethe’s theory does not include nuclear energy loss.
2. For electronic stopping, its range of validity, determined by the underlying first Born approximation, shrinks rapidly with increasing $Z_1$.
3. Screening by electrons bound to the projectile and charge exchange are not foreseen in the Bethe theory,
4. Even for the lightest ions, quantitative predictions require corrections in the keV and lower-MeV regime,
5. Little quantitative information was available in 1960 about the main parameter characterizing the material, the so-called $I$-value.

6.1. Nuclear Stopping

Nuclear stopping is closely related to the cross section for elastic scattering and a prime issue in radiation damage and sputtering. At the time when I entered the field of radiation physics, in 1962, elastic scattering of heavy particles was described in principle by a Yukawa-type potential introduced by Niels Bohr [17]. For the purpose of deriving a differential cross section this potential was approximated either by an inverse-square potential which led to a stopping cross section independent of the beam energy, or by a billiard-ball interaction which led to a differential cross section independent of the transferred energy. It was not clear how either approximation was related to Rutherford scattering which had to be the appropriate description at high energies and large scattering angles.

A powerful solution to this problem was found in what is known as the LSS theory, which is a bunch of four papers by Lindhard and coworkers published in the 1960s [50, 16, 15, 51]. Nuclear scattering and stopping was treated in ref. [51]. On the basis of Thomas-Fermi-type interaction potentials, scaling laws for elastic scattering were derived which expressed the differential cross section as well as the stopping cross section each by a single curve dependent on the adopted screening function and screening radius.

Quantitative improvements were made subsequently, mainly on the basis of revised estimates of scattering potentials combined with numerical evaluation of scattering integrals. It is, however, not a simple task to check the validity of such approaches by direct measurements. For details I refer to ref. [42] Ch. 6.

6.2. Ion Ranges

Ion ranges used to be measured in cloud chambers, initially for products of radioactive decays, alpha and beta particles, where the energy loss is well characterized in terms of electronic stopping. After the discussion of nuclear fission, measurements were made also with the fragments of fission events, where nuclear stopping contributes [52, 53].

The initial motivation for the LSS theory was the need for a theoretical scheme to combine electronic and nuclear stopping in a theory of ion ranges valid over a wide range of ion-target combinations and beam energies, in particular for fission fragments. In addition to a description of nuclear stopping this required a characterization of electronic stopping in a velocity range
where the Bethe theory does not provide a valid description. I shall come back to this point below, but at this stage I just mention that several theoretical approaches, including those by Firsov [54] and Lindhard & Scharff [50], led to the characterization of electronic stopping by a friction-like force proportional to the beam velocity.

On this basis the LSS theory provided estimates of the average traveled pathlength and its fluctuation, expressed as a set of curves characterized by one single parameter, in terms of appropriate scaling variables for energy and pathlength [15]. This work also allowed to include deflection by elastic collisions via the concept of a projected range.

A parallel paper [16] describes the sharing between the energy deposited in nuclear and electronic motion, respectively. This is essential in the description of radiation effects, where energy deposition in nuclear motion was thought to account for displacement damage and sputtering, whereas energy deposition in electronic motion was thought to account for ionization phenomena and emission of photons and electrons. While this separation is valuable and often justified, possible exceptions were already mentioned in the original paper [16] but came to represent new physical phenomena much later. More about this in Sect. 7.8.

The physical basis of the LSS theory, i.e., separation of scattering processes into elastic scattering and electronic stopping, has been a dominating principle in ion beam physics for over 50 years. All Monte Carlo and binary-collision simulation codes build on this principle. The popular TRIM code [55] is essentially an implementation of the LSS theory with a modified universal potential. The range of applicability of TRIM was expanded by incorporation of electronic stopping cross sections for beam energies above the stopping maximum [56]. This code is now known as SRIM.

6.3. Low-Velocity Electronic Stopping

The electronic stopping cross section is known to go through a maximum, often called Bragg maximum, and the term ‘low-velocity’ is meant to denote the energy range below that maximum.

Electronic stopping in the LSS theory was quantified in terms of an expression found by Lindhard & Scharff on the basis of dielectric theory [5] and a Thomas-Fermi model of scattering. The formula was derived in the late 1950s and very similar to an expression found independently by Firsov [54]. Only the final result was ever published [50]. A detailed analysis was given by Tilinin [58].

Lindhard’s and Firsov’s expressions both predicted velocity-proportional, friction-like stopping and, originating in the Thomas-Fermi model, suggested a smooth dependence of the stopping cross section on \( Z_1 \) and \( Z_2 \). It therefore came as a surprise, when measurements by Ormrod & Duckworth [59] showed ‘\( Z_1 \) oscillations’ in electronic stopping cross sections for a series of ions in carbon. This caught the interest of theoreticians. Since the amplitudes of the observed oscillations were moderate [60], attempts to understand their origin took either the Firsov or Lindhard-Scharff formula as a starting point, with limited success.

The real shock came at ICACS-2 with Eisen’s measurements on silicon crystals under channeling conditions (Fig. 14), with an order-of-magnitude variation from minimum to maximum. An explanation came shortly after from Lindhard in terms of the Ramsauer effect in electron-atom scattering. Indeed, in a moving reference frame stopping can be understood as the momentum transfer from a cloud of electrons passing by. At low electron velocities, the cross section is sensitive to the electronic structure of the scattering center.

Unfortunately, Lindhard’s idea has only been published in a M.Sc. thesis by his student J. Finnemann [61]. The idea was taken up later by Briggs & Pathak [62]. While these calculations
are based on realistic electron densities, the underlying formula for the transport cross section fails to deliver the correct velocity dependence [42]. This error, which propagates through a series of papers by Pathak, got unnoticed, since comparisons with measurements were performed only over a narrow velocity interval. Subsequent evaluations of the correct formula by several groups all showed pronounced $Z_1$ oscillations, but quantitative agreement with experiment was achieved only in rare cases [63].

An interesting tool is an extended Friedel sum rule [65] which, for a Fermi gas, delivers stopping cross sections with $Z_1$ oscillations that decrease in amplitude with increasing energy. The well-known Friedel sum rule [66] sets a restraint on the phase shifts for target electrons scattered on an external charge embedded in a Fermi gas, based on charge equilibrium. However, a proof of the extended Friedel sum rule from basic principles is still missing.

An intriguing question concerns the existence or non-existence of $Z_2$ oscillations. Such oscillations are wellknown but rather weak in high-velocity stopping [67, 68]. A potentially useful tool to study this feature at low speed is the reciprocity principle for low-speed stopping cross sections [64], $S(Z_1 \text{ in } Z_2, v) = S(Z_2 \text{ in } Z_1, v)$, which is exact for neutral projectiles in dilute gases but approximately fulfilled also for solids (figure 15). Figure 16 compares measured stopping cross sections for numerous ions in carbon with the corresponding quantity for carbon ions in a number of target materials. There are similarities, in particular in the range from Al to Cu, but there are also differences, part of which are due to experimental uncertainties e.g. for C-Be.
Figure 15: Color online. Reciprocity in low-velocity stopping. Stopping cross sections for C in Si (blue symbols, upper five data in legend) and Si in C (red symbols, lower five in legend). As to be expected, deviations from reciprocity are found in the high-\(v\) end of the graph, where projectiles are no longer neutral. From [64].

6.4. Stopping of Light Ions

As mentioned already, the standard of reference in light-ion stopping is Bethe’s stopping formula from 1930 [74] together with a relativistic extension [75]. This formula is based on the Born approximation to describe the interaction between a point charge and the target electrons and an asymptotic expansion valid for high projectile speed. Attempts to avoid the latter, purely mathematical approximation, or at least to go to higher-order expansions, were made from the early 1950’s on [76].

6.4.1. Shell Correction

The need for a correction, called shell correction, is illustrated in figure 17. It is seen that most of the experimental data available in 1953 fall into a velocity range where the logarithmic factor \(L\) in the Bethe formula (2) deviates significantly from the measurements. At the same time, little theoretical knowledge was available about the \(I\)-value, except Bloch’s finding [77] that \(I\) was approximately proportional to \(Z_2\). Therefore, predicting stopping cross sections required experimental data for \(I\), and finding \(I\) from experimental data required shell corrections. Moreover, since \(I\) enters into a logarithm, precision measurements and accurate shell corrections were needed to allow reliable determinations of \(I\).
Much experimental and theoretical work has been devoted to this issue. For a survey I refer to ref. [78] ch. 6. Here I mention a major achievement on the experimental side. H. H. Andersen et al. [79] reported stopping measurements for protons and deuterons with an accuracy around 1%, which was unheard of at the time and which has not been beaten during the 50 years that have passed since then. This high accuracy was achieved by measuring the deposited energy via the heating of a target cooled to liquid helium temperature. I-values extracted from such measurements [68] form the basis for standard tables such as refs. [72, 80]. Calorimetry has become a standard technique in particle detection from the late 1970s [81]. Asymptotic expressions for shell corrections were given by Fano [49]. Shell corrections beyond an asymptotic expansions were developed by Bonderup [82]. A rather general scheme, valid for both free and bound electrons, was developed in ref. [83].

6.4.2. Barkas-Andersen and Bloch Correction

According to the Bethe formula (2) the stopping cross section should be proportional to $Z^2$ over the entire range of validity. Figure 18 shows that this relation, which implies the stopping cross section of bare He ions to be 4 times that of bare H ions, is not strictly fulfilled. The magnitude of the measured deviation, $\lesssim 1.5\%$, indicates a landmark in the field of stopping, as is evident from Fig. 19, which demonstrates that the effect becomes more than an order of magnitude more pronounced at lower energies. That graph shows the stopping of antiprotons compared with that of protons. The common feature of the two graphs is that both effects can be explained in terms of a $Z^3$ correction to the Bethe formula, as suggested previously [84] in
connection with range measurements on positive and negative pions.

The measurements from ref. [70] generated numerous theoretical studies, an activity still going on. Pioneering was the work of Ashley et al. [85], which was an extension of Bohr stopping theory to the next order in $Z_1$. This theory implied that deviations from straight Coulomb scattering were to be found in distant collisions. While the validity of these calculations has been generally accepted, the assumption of a negligible effect from close collisions was questioned by Lindhard [86] who, in addition to an alternative estimate of the $Z_1^3$ correction, pointed out that another correction from close collisions had to be expected according to the Bloch stopping formula [87].

Bloch’s work was originally understood as an important link between classical [88] and quantal [74] stopping theory. The main point here is that the Bohr formula does not predict a strict $Z_1^2$ dependence of the stopping cross section. Therefore a correction to the Bethe formula must occur in the transition from Bethe to Bohr stopping. This correction is $\propto Z_1^4$ in the leading order in $Z_1$.

Obviously, $Z_1^3$ and $Z_1^4$ corrections are the lowest terms in an expansion in powers of $Z_1$. 
More recent theories [78] do not operate with such expansions. Therefore we now speak about Barkas-Andersen (or just Barkas) corrections, which change sign for negative projectile charges, and Bloch corrections, which do not depend on the sign of the charge.

With regard to the controversial issue of the importance of close collisions, there is general agreement as far as the existence of the effect at low impact parameters is concerned. With regard to the relative weight, two independent calculations in which I have been involved, indicate that close collisions well may be dominating [89, 90].

6.4.3. Screening and Threshold Effects

The Coulomb force is a long-range interaction, and the stopping cross section for free-Coulomb scattering is known to diverge. In Bohr and Bethe stopping theory the stopping cross section is finite since a lower limit on allowed energy transfers is set by atomic binding of target electrons. Studying stopping in a free-electron metal, Kramers [93] recognized that in a free-electron gas, the interaction range is limited by screening via target electrons to within an effective screening radius $\nu/\omega_P$, where $\omega_P$ denotes the plasma frequency.

Both in the original paper [5] and a later followup [94], Lindhard used the stopping of a point charge in a Fermi gas as an illustration. Stopping cross sections of arbitrary atoms were determined by applying the Thomas-Fermi principle, i.e., electron clouds around target atoms were treated as Fermi gases with an electron density varying in space (local density approximation) [69].

As stated in Sect. 1, the basic formalism established in ref. [5] is a landmark in theoretical physics, and its application to stopping in a Fermi gas provides useful insight. Application of
the local density approximation [69] was a useful step at a time when more powerful tools were not available. However, already in 1967, in a thorough analysis of this scheme, Bonderup [82], proving its usefulness in the determination of shell corrections, found that calculated $I$-values deviated significantly from measured ones.

I like to emphasize that there is no reason to restrict the application of Lindhard dielectric theory to a Fermi gas. This is wellknown in condensed-matter theory, while only few attempts have been made to develop alternative models in particle penetration. Together with Belkacem [95] I applied the scheme to a gas of harmonic oscillators. The mere fact that such a system is characterized by two material parameters (resonance frequency and electron density) instead of just one led to interesting conclusions which I shall come back to in Sect. 6.4.5.

The question of the existence of a genuine threshold energy for electronic stopping has interested experimentalists and theorists for at least half a century [96]. Since theory does not predict a threshold for stopping in a Fermi gas, interest has been directed toward insulators and semiconductors. The central point is that, unlike in electron penetration, where a projectile with $v \simeq v_0$ can lose all its energy in a single collision, there is lots of energy available for excitation/ionization by a heavy projectile at low velocities where the energy transfer to target electrons gets down to a few eV.

The question of whether or not this energy can be transferred to a target electron is not trivial and has proven to require tools from solid-state physics to answer [97]. Strong evidence for a genuine threshold of electronic energy loss in high-bandgap insulators was presented by Markin.

Figure 19: Stopping of antiprotons in silicon. From [71]. Solid line: Proton stopping [72]. Dashed line, low-velocity calculation for antiprotons [73]. From [71].
et al. [91]. Their results, shown in Figure 20 for the case of LiF, together with experimental findings by other groups triggered considerable activity on the theoretical side.

6.4.4. Polarization Field (Wake)

The polarization field of a point charge moving through a medium was discussed by Fermi [98] in connection with the so-called density effect in the energy loss of relativistic charged particles in matter. Niels Bohr [17] presented a sketch (figure 21) which indicates the similarity of the induced charge with the wake generated by a boat moving swiftly through water. Evidently, the induced field provides the stopping force on the projectile.

Nelaavathi et al. [99] evaluated the polarization potential for a simple model of an electron gas and demonstrated the existence of oscillations in space that reach far beyond the screening radius characterizing the short-range interaction.

This observation generated a large number of theoretical and experimental studies. In the original paper [99] it was suggested that valleys in the wake potential could bind target electrons, ‘wake-riding electrons’, which should show up as ‘convoy electrons’ in the spectrum of electrons emitted from a surface. While convoy electrons moving with the beam velocity are indeed observed in the flux of electrons emerging on the far side of a foil, the same phenomenon is also observed in atomic collisions in dilute gases, where the polarization field of the medium is
§ 3.1. The Penetration of Atomic Particles through Matter.

Fig. 6. adiabatic limit, the positions of the electrons will exhibit complete symmetry with respect to a plane through the particle perpendicular to C, and these electrons will, therefore, give rise to no resultant force on the particle. Inside the adiabatic limit, however, there will be a closer approach of the electrons to the line C behind the particle than in front of it, and these electrons will, therefore, create an electric field directed against the motion of the particle.

To estimate the strength of the field, we may simply calculate the electric charge accumulated in the "wake" of the particle, represented by the cone A containing the atoms for which the collision is practically completed. Since a measure of the displacement of a free electron in a collision for which \( p \gg b \), according to the considerations in § 1.1, is given by \( b \), the surplus charge in a section of the cone at distance \( x \) behind the particle and of thickness \( dx \) will be roughly \( 2\pi Nbxdx \), where, as above, \( N \) denotes the number of atoms per unit volume. For the attractive force of this charge on the particle we, thus, have approximately

\[
F \approx 2\pi b N x \quad (3.1.12)
\]

Figure 21: Schematic illustration of the motion of bound electrons induced by a penetrating charged particle. The symbol \( C \) denotes the trajectory, \( d \) the adiabatic radius which is \( \propto v \), and \( l \) the approximate borderline between close and distant collisions, which is \( \propto 1/v \). From [17].

Figure 22: Color online. Stopping ratio \( R \) between the stopping cross section per atom in a dicluster and an isolated proton in a gas of harmonic-oscillator atoms. The ratio \( \omega_P^2/\omega_0^2 \), where \( \omega_P \) represents the plasma frequency and \( \omega_0 \) the resonance frequency of an individual oscillator, is a measure of the density of the medium. From [100].

negligible. Here, pertinent processes are ‘electron capture into the continuum’ or ‘electron loss.
into the continuum’.

Indeed, while the existence and oscillatory nature of the wake potential has never been questioned to the author’s knowledge, its significance is mostly related to the immediate neighborhood of the projectile [101]. Some evidence for oscillatory effects at larger distances from the projectile has been found in experiments with dclusters penetrating two foils [102, 103], but more often, wake potentials have been asserted to be responsible for physical effects that are only loosely related to polarization phenomena. An example is discussed in the following section.

6.4.5. Stopping of Clusters

In 1982, Ratkowski et al. [104] found an enhancement of the stopping cross section per atom for penetrating H$_2^+$ and H$_3^+$ clusters as compared to that of a single H$^+$ ion. Although the effect was shown later to be smaller [105], its existence has never been questioned. Calculations to model this effect have often been performed within the Lindhard formalism for a Fermi gas [106], and such calculations can be conveniently made by use of the polarization field which provides the stopping force on the atomic ions making up the cluster. This has led to the widely-spread opinion that this ‘proximity effect’ in the stopping of cluster ions is caused by the polarization wake.

Figure 22 shows that the opposite is true in the velocity range where measurements have been made, i.e., the high-$v$ part: There the proximity effect is most pronounced in a dilute gas where there is no wake. Unlike the free-electron gas, the dielectric function [95] of an oscillator gas allows independent variation of the binding frequency $\omega_0$ and the plasma frequency $\omega_P$. Thus, variation of the ratio $\omega_P^2/\omega_0^2$ is a measure of the significance of wake effects, and the most pronounced proximity effect, expressed by the stopping ratio $R$ is found for the lowest density [100]. The low-velocity portion of Figure 22 the oscillating behavior is determined by the time delay in the passage of the trailing relative to the leading proton.

6.5. Stopping of Heavy Ions

6.5.1. Charge-State Paradox and Effective Charge

In the introduction I mentioned measurements by Lassen [4], which showed a pronounced gas-solid difference in the equilibrium charges of penetrating fission fragments (Fig. 3). An explanation of this effect was offered by Bohr & Lindhard [108], who asserted that an ion penetrating through solid matter tends to be in an excited state because of frequent encounters with the target atoms and therefore has a higher cross section for ionization. Such excitations will decay if the time between successive collisions exceeds the lifetime of the state. This condition will normally be fulfilled for a sufficiently dilute gas, but not necessarily in condensed matter.

Figure 23 confirms this gas-solid difference for I ions in Ar and C, but it also shows the rather surprising result that this difference does not seem to affect the energy loss: The experimental points reflect so-called effective charges, i.e. measured stopping cross sections normalized to $Z_i^2$ times the stopping cross section for protons at the same speed in the same target. Effective charges for solid and gaseous targets are seen to coincide within experimental scatter, while the real charges differ by up to a factor of two.

Betz & Grodzins [112] asserted that these data contradicted the Bohr-Lindhard theory [108] and proposed that there was actually no notable difference between ion charges penetrating through gases and solids. Measured differences were asserted to be due to Auger decays taking place between the point of the emergence from the solid medium and the arrival at the detector.

These findings generated a lively debate for almost 30 years. On occasions it involved discussions about fundamental questions about how actually to define the charge of an ion under
Figure 23: Ions in argon and carbon. Solid line: Mean equilibrium charge in carbon. Dashed line: Mean equilibrium charge in argon. Triangles: Effective charge in argon. Circles: Effective charge in carbon. From [107].
penetration through a medium. Sophisticated experiments were undertaken with the purpose to experimentally determine the state of excitation of a penetrating ion from emitted-x-ray spectra [113, 114].

Regarding the model by Betz and Grodzins, a search for Auger electrons emitted from the far side of the foil showed an electron yield far below what was needed to explain the observed difference in the ion charge [115].

Before going to the resolution of the charge-state paradox, a word is necessary about the effective-charge concept which, in its common form, was proposed by Northcliffe [116]. It rests on two assumptions,

- that the stopping cross section of a bare heavy ion with an atomic number $Z_1$ is identical with the stopping cross section of a proton multiplied by $Z_1^2$, and
- that the stopping cross section of a screened heavy ion with charge number $q_1$ is found by replacing $Z_1^2$ by $q_1^2$.

Although neither of these two assumptions is generally fulfilled, the scheme allows to extract a charge number from measured stopping cross sections, provided that the stopping cross section of a proton is known. However, the charge number of a screened ion so defined turns out to be significantly lower than the measured ion charge. While the origin of this discrepancy was
unknown for several decades, the practical consequence was to distinguish between an ‘effective charge’ and an ion charge. The origin of the discrepancy is to be sought in the transition from Bethe to Bohr stopping theory which, for a heavy ion interacting with a target electron, i.e., for \( e_1 = Z_1 e \) and \( e_2 = e \), lies around \( v = 2Z_1 v_0 \) according to the Bohr criterion eq. (1). For a proton that transition lies around \( v = 2v_0 \), i.e., at a lower projectile speed. At the same time, screening is significant for \( v \lesssim Z_1^{2/3} v_0 \). This implies that the energy range where screening is important lies mainly within the Bohr regime. Thus, the difference between the effective charge and the ion charge is only weakly related to screening but mostly due to the transition from Bethe to Bohr stopping theory [119].

Figure 24 shows the case of oxygen. If the effective-charge scheme were valid, the plotted quantity would be a horizontal line at the stopping ratio 1. The blue dashed line, which represents the ratio of the stopping cross sections of a bare oxygen ion and a bare helium ion, demonstrates that most of the difference to the horizontal line is accounted for by the transition from Bethe to Bohr stopping theory. The difference between the dashed and the red solid line represents the effect of screening. The graph also shows that binary stopping theory [120], to be mentioned in the next section, describes the overall behavior quite well.

Coming back to the charge-state paradox, the lack of Auger electrons suggests that the gas-solid difference in the equilibrium charge is indeed explained by the Bohr-Lindhard model. This requires that an explanation be found for the rather weak dependence of the stopping cross section on the ion charge. Maynard et al. [121] demonstrated that the combined effect of projectile screening and higher-order corrections leads to a charge dependence much weaker than the previously assumed \( q_1 \) relation. This view is fully supported by more recent theories [110, 122].

Although figure 23 appears to deny a gas-solid difference in stopping, subsequent measurements [123, 124, 125] demonstrated that stopping cross sections indeed tend to be greater in solids than in gases, if differences in atomic number are taken into account properly.

6.5.2. Stopping Theory

Stopping theory for swift heavy ions has been developed from the mid 1990s and can now be considered to be a mature field which does not any longer depend on empirical concepts such as the effective charge. I have given a systematic review in two monographs [78, 42] and a more recent survey in ref. [111], to which the interested reader is referred. At this point I like to mention that the theory falls into two independent parts,

I) Stopping of heavy ions in the relativistic regime. In its present form this theory was developed by Lindhard and Sørensen [126], based on relativistic Coulomb scattering, going over the transport cross section and ending up in a correction to the relativistic Bethe formula [75]. Deviations from straight Coulomb scattering due to the finite size of the projectile nucleus are taken into account, and successful comparisons with experimental data have been made [127].

II) Predictions of electronic stopping of screened heavy ions can be made primarily by four different schemes specified in table 1.

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2In published stopping tables like ref. [117, 118] stopping cross sections for helium were employed for the normalization instead of hydrogen.
Table 1: Theoretical schemes quantifying stopping of screened ions. Terms ‘high’ and ‘low’ v ref to above and below the electronic stopping maximum. From [111].

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Ref.</th>
<th>Code</th>
<th>Target</th>
<th>Starting at</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary Theory</td>
<td>[110]</td>
<td>PASS</td>
<td>Atom</td>
<td>Bohr</td>
<td>High v downward</td>
</tr>
<tr>
<td>PCA/UCA</td>
<td>[128]</td>
<td>CasP</td>
<td>Atom</td>
<td>Bethe-Bloch</td>
<td>High v downward</td>
</tr>
<tr>
<td>TCS-EFSR</td>
<td>[129]</td>
<td>HISTOP</td>
<td>Fermi gas</td>
<td>Quantal</td>
<td>Low v upward</td>
</tr>
<tr>
<td>SLPA</td>
<td>[130]</td>
<td>LDA</td>
<td>Quantal</td>
<td></td>
<td>High v downward</td>
</tr>
</tbody>
</table>

All schemes have strong and weak points. Our PASS code [120], covering a velocity range from $\sim v_0$ well into the relativistic regime (through the incorporation of the Lindhard-Sørensen term) covers the widest energy range. The CasP code [122] is the only one accessible on the internet\(^3\), and it covers the nonrelativistic velocity range from around the stopping maximum upward. The HISTOP code [129] is the only one accounting for $Z_1$ oscillations. The SPLA code [130] has a potential but makes use of a ‘shellwise local plasma approximation’ which appears hard to justify from first principles.

7. Sputtering

The fact that figure 1 does not show activities in sputtering between 1940 to 1945 should not be misunderstood: The phenomenon of sputtering was discovered in 1852, and there is ample documentation in the literature of activities in basic as well as applied research until the beginning of World War II. Typical beam energies were well below and very rarely above 1 keV per ion. For a brief survey of the early development the interested reader is referred to ref. [131]. For comprehensive reviews I refer to a series of four books edited by R. Behrisch starting with [132, 133, 134, 135] and a later recent survey edited by myself [136].

7.1. Sputter Emission

A key problem, widely debated over almost a century was the very nature of the emission process. There were essentially two alternatives, local evaporation from a ‘hot spot’ heated by a bombarding ion, or momentum transfer from the projectile to an atom, resulting in a cascade of atomic collisions. After the discovery of spot patterns reflecting the crystal structure of the bombarded target by Wehner [3] (figure 2), momentum transfer got rapidly accepted as the dominating mechanism. Here it was tacitly assumed that the evaporation pattern from a single crystal would not show such spots. Experimental confirmation of this crucial assumption actually came ten years later\(^4\) [138].

From a present-day point of view, the main difference between a hot spot and a collision cascade is the density of atoms in motion and their energy. This means that there must be a smooth transition between the two extremes, but this was recognized only two decades later.

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\(^3\)An internet version of the PASS code will be available shortly
\(^4\)Actually, the crucial experiment had already be done by Knudsen in 1917 [137], but inspection of the Web of Science indicates that this paper had been unknown in the community.
7.2. Sputter Yields

Sputter rates, i.e., the mean number of atoms emitted per unit time, had been measured from the late 1880s, but measuring sputter yields, i.e., the mean number of atoms emitted per incoming ion, required to control the fluence of incoming ions. Figures 25 and 26 show the results of measurements at eV and keV energies for several target materials with large variations from element to element. These variations were found to anticorrelate with the sublimation energy of the material, i.e., a quantity closely related to the surface barrier which an atom has to overcome in order to get sputtered.

Refs. [139, 140] and related papers by these two groups formed a comprehensive experimental basis for the exploration of sputter processes in the 1960s. This includes sputter yields as a function of $Z_1$ and $Z_2$, the beam energy and the angle of incidence. Figure 27 shows an example, comparing sputter yields vs. beam energy of various ions on copper. While the absolute magnitude of the yield is seen to increase with $Z_1$, the energy dependence is characterized by an increase up to a certain maximum and a decrease at higher energies. Almén & Bruce quote an assertion by Rol et al. [141] that the sputter yield should be proportional to the energy deposited in a shallow surface layer, i.e., the nuclear stopping cross section $S_n$. A few years later, with the appearance of the LSS theory, a quantitative expression for $S_n$ became available which was
7.3. Energy Spectrum of Sputtered Atoms

A central quantity in an attempt to understand the emission process must be the energy distribution of emitted atoms. Since the sputtered flux consists predominantly of neutral particles, this was not easy to measure. The first successful attempt was due to Thompson [143], who developed an impressive setup to measure a time-of-flight spectrum shown in Figure 28, making use of a rotating mirror providing the start signal and neutron activation to measure the spatial distribution of deposited material. Measurements were performed on gold and analyzed in ref. [144].

In this context, two central theoretical papers need to be mentioned. In ref. [145], Robinson derived an inverse-square relation for the collision density in an elastic-collision cascade, i.e., a quantity closely related to the energy distribution of recoiling atoms. Subsequently, Robinson [146] demonstrated how to make use of the Laplace transform to solve transport equations governing collision cascades for cross sections more realistic than for billiard-ball scattering.

Combining the inverse-square spectrum with a planar surface barrier, Thompson [144] concluded that the energy spectrum of sputtered particles had an inverse-square-like tail at high energies and a maximum in the energy range of the surface binding energy, in agreement with the measured spectrum of gold.

found to confirm this assertion [142].
when the penetration depth of the impinging particles is taken as a scale. The target was water-cooled and temperatures very seldom exceeded 100°C. When materials with low melting points, e.g. Sn and In, were used, the beam had to be swept over the target in order to decrease the current density. Otherwise the foil was burned through.

8.3. Sputtering Ratios Versus Ion Energy

Figs. 19a and 19b show the sputtering ratio as a function of ion energy for noble gas ions Ne, Ar, Kr and Xe, bombarding on Cu and Ag. Sputtering for Copper and Silver is also indicated in the diagrams. We note that for N, Ne and Ar ions, S is fairly constant, when the ion energy is higher than 5 keV, corresponding to a penetration depth of about 10 μg/cm² S even decreases slightly for Cu. For heavier ions sputtering increases with energy within the whole energy range. However, a maximum may be expected for a sufficiently high ion energy. In the sputtering diagrams sputtering ratios determined by Roloff (×) and by Keywell (○) are indicated and the agreement with our measurements is very good.

In figs. 20a, 20b and 21 sputtering ratios for some other materials are given. Here we observe that S becomes constant above ion energies varying from 10 to 30 keV. On Sn we got a considerably decreasing sputtering ratio with increasing ion energy until we detected that in this case S also depends on the power dissipated in the Sn foil. When we used the same power throughout the experiment we measured the sputtering given in fig. 20b. It is interesting to compare fig. 19b with figs. 20a, 20b and also with fig. 21. All the target materials have practically the same mass number M², about 100. Not only does the sputtering ratio vary considerably for different elements, but the shapes of the curves also are quite different. This indicates a complicated influence of the properties of individual elements on sputtering. A complete theory of sputtering must be able to explain all features indicated here. However, as to be shown in § 9 it is possible to calculate sputtering ratios approximately for noble gas ions bombarding on solids.

8.4. Current Density

For Cu and Ag we have measured the sputtering ratio at different current densities of 45 keV Kr ions. The metal foils used were first bombarded at high current densities to remove the surface layer. After that, three targets were bombarded using the mass numbers 89, 84 and 86, respectively. If we

7.4. Wehner Spots

With the acceptance of the momentum-transfer model of the sputter process the question arose how to explain spot patterns like the one shown in figure 2. A solution offered by Silsbee [147] is shown in figure 29. This represents a modification of a classical demonstration of momentum transfer by a series of aligned balls, with the sole difference that the initial impulse is not given parallel to the row. Silsbee demonstrated that momentum gets focused if the free distance between the balls is less than their diameter.

Silsbee’s model was subsequently refined and expanded considerably: Hard-sphere scattering was replaced by a more realistic scattering potential [149], row atoms did not need to lie exactly on a straight line [150], and neighboring rows could assist the focusing process [151]. Focusons also turned out to be the main issue in the first molecular-dynamics simulation in the field of atomic collisions in solids [152].

While it was clear that focusons had to be attenuated via energy lost in individual atom-atom collisions, theoretical estimates of the energy range where collision sequences could be focused, as well as the maximum range of focusons, were found to depend sensitively on the (poorly known) interatomic potential.
At the same time, focusons played an increasing role in the interpretation of radiation damage experiments. When measurements showed that lattice defects were generated far deeper than the penetration depth of the ion beam, focusons tended to be invoked as a possible explanation [153]. Postulated attenuation lengths of tens and hundreds of nanometers were common in those days.
but unsupported by theory. Remind that Wehner’s spots had been found at beam energies as low as 50 eV, where ions do not penetrate deeper than 2-3 atomic layers. Although spots were also found in sputter experiments at energies where ions penetrate deeply into the target [154, 155], the need for a process involving the near-surface area was evident but not generally recognized.

It was actually Jens Lindhard, who asked me at the time whether it was necessary to invoke the bulk structure at all in the explanation of spot patterns. Figure 30 illustrates one of two mechanisms that I found together with Lehmann [148]. It involves only two atomic layers but takes into account the binding energy to the target surface. If a surface atom is kicked off by a subsurface atom along their connection line, it will take over most of the kinetic energy, but if it is knocked on at an angle, energy will be lost so that the surface atom may not be able to overcome the barrier. As mentioned in the previous section, we had learned from Robinson [145] that the recoil spectrum in a collision cascade is an inverse-square law. This means that the majority of the atoms in a cascade have energies not far above the surface binding. The two features together ensure a rather narrow peak of the ejected intensity around the nearest-neighbor direction, regardless of whether or not there is a string of atoms underneath.

Our paper [148] generated lively discussion: An important point was that it provided an explanation for spots observed in hexagonal metals in directions were there were no straight lattice rows [156]. Those spots were not markedly different from those observed in face-centered cubic metals where, in principle, long-range foci could contribute to sputtering.

Actually, since spot patterns were the experimental evidence that led to the proposal of the focuson concept, it appeared justified to ask whether focusons existed at all. The straightforward answer to such a question would have been a realistic computer simulation of the process, preferably by molecular dynamics. Despite the pioneering work of Vineyard and colleagues...
mentioned above, this had to wait for a quarter of a century.

| Figure 31: Sputter yields of Cu for noble gases compared with predictions from linear cascade theory, implying an energy dependence proportional to the nuclear stopping cross section $S_n$. Solid line: $S_n$ according to [51]. Dashed line: Low-energy approximation based on Born-Mayer (exponential) ion-target interaction potential with constants from [157]. From [158].

7.5. Linear Cascades

The question remained whether a model for sputtering that denied a significant contribution of long-range focusons was able to quantify measured sputter yields. The answer was to develop a sputter theory based on random collision cascades.

Figure 31 shows a comparison between measured sputter yields on copper, available in 1969, and a simple formula derived by the present author on the basis of linear transport theory. The underlying framework was the LSS theory by Lindhard and coworkers [15, 51], in particular the use of backward transport equations, range concepts, and the power cross section that enables analytic evaluation by the Laplace technique mentioned above [146]. The step from ion range to deposited-energy distributions and higher moments involved J. B. Sanders [159]. The full theory predicted sputter yields and related quantities for a variety of geometries.

The theory was followed up in a monumental experimental effort by H. H. Andersen & H. L. Bay. They addressed many aspects of sputtering, in particular experimental problems with yield measurements, and they generated an extensive collection of measured sputter yields for numerous ion-target combinations [160].

7.6. Complications

An important finding was the dependence of the sputter yield on the ion fluence. A first indication of this effect emerged from measurements by Almen & Bruce [18] shown in the Fig. 32.
For some investigations it is necessary to have the same current density over the whole target. In such cases we modulate the ion beam by means of a saw-tooth voltage on two deflection plates, placed at the entrance side of the separator magnet (see ref. 1). High quality insulators, carefully protected from the plasma. Where suitable chemical compounds do not exist, and the elements themselves have a low vapour pressure, the elements have been handled in a sputtering ion source. Concerning ion source problems see ref. 4.

Our sputtering results at 45 keV ion energy are reproduced in fig. 1. We used Cu, Ag and Ta as target materials because foils of high quality can be obtained commercially. The current density was 10-100 μA/cm² and the pressure in the target chamber was 0.8-1.5 × 10⁻⁵ mm Hg. Usually we sputtered off more than 200 µg/cm², but in some cases lower amounts had to be accepted, since the sputtering ratio can be very low. It can also be ~) K. O. Nielsen, Nucl. Instr. 1 (1957) 289. 4) j. Druaux and R. Bernas, Proc. 1955 Harwell Isotope Conf., Ch. 4.

Pronounced variations were reported of the measured yield between ions of similar atomic number $Z_1$. Yields very close to zero were found for some ions. Those cannot be explained in terms of collision theory but indicate the formation of layers with a changed chemical composition and eventually a negative sputter yield. Figure 33 shows sputter yields of copper as a function of ion fluence [161]. The experimental technique, where the target is mounted on a quartz microbalance, the resonance frequency of which records the weight loss, enabled measurements at low fluences leading to low concentrations of implanted ions.

It is seen that sputter yields may depend significantly on the bombarding-ion fluence, most pronouncedly so in the case of bismuth ions. A noticeable fluence dependence is also observed for self-sputtering, i.e., bombardment with Cu ions, indicating either the presence of an initial impurity layer or bombardment-induced changes in surface structure.

One may conclude from these measurements that comparisons between measured and calculated sputter yields are meaningful only for equivalent target conditions. In other words, comparison of calculated yields referring to a clean planar target surface require measurements under ultrahigh vacuum close to zero fluence.

Figure 33 represents an aspect of a major group of phenomena comprising sputtering of alloys and compounds including isotope sputtering, desorption of surface layers, ion beam mixing and depth resolution of sputter profiling [162]. Figures 32 and 33 give an impression of the degree of complexity inherent in these topics. Any researcher studying or applying sputtering has to cope with at least one of these items, and the literature on every single of them is enormous. Because of processes taking place on very different time scales such as diffusion and/or segregation, predictive theories of alloy sputtering and/or ion-beam mixing are not yet available.

Rather than going into details here I like to touch on a related topic. Sputter theory suggests...
a cosine distribution in the emission angle for polycrystalline targets and energies in the keV regime [158]. In practice, both minor and major deviations from this behavior are observed, dependent on ion type and energy as well as bulk and surface structure of the target. In multi-component materials, emission patterns may be studied separately for every component. If, as an example, species A is enriched in the surface of an AB alloy, sputtered B atoms tend to originate in deeper layers than sputtered A atoms. This will produce a narrower angular distribution for species B [163]. This effect has been utilized by H. H. Andersen and coworkers [164] to demonstrate the presence of segregated layers in ion-bombarded CuPt alloys.

7.7. Nonlinear Sputtering

The experimental confirmation of an inverse-square energy spectrum of the sputtered flux provided strong support to an explanation of sputter processes in terms of the momentum-transfer model. After all, a Maxwellian spectrum would have to be expected for evaporation from hot spots. Two discoveries indicated that this was not the full truth. Going back to figure 31 you may notice a significant difference between the shape of the theoretical curve and the data in case of Xe bombardment and, less pronouncedly, for Kr. This could, in principle, be due to the choice of the nuclear stopping cross section, but this appeared unlikely, since the difference is most pronounced at high energies, where the cross section is close to Rutherford’s law.

In view of a pronounced enhancement near the maximum of the nuclear stopping cross section, the question came up whether this enhancement was due to high density of deposited energy. In
an experimental study, Andersen & Bay [12] compared the sputter yield for Te\(^+\) with that for Te\(_2^+\) at the same velocity (or energy per atom), with the surprising result that the sputter yield per incident atom was enhanced for bombardment with the molecule. This result was incompatible with linear transport theory.

A simple estimate on the basis of cascade theory [167] indicated that energy densities in heavy-ion bombardment could quite well come up to more than several eV per atom and, hence, could lead to sputter emission. Amongst several estimates of sputter rates based on heating of a spherical or cylindric region by an incident beam I like to mention ref. [168].

Measurements of the energy spectrum of sputtered particles received increased interest in this context. It was clear that a possible Maxwellian could not be identified in the tail of the spectrum.
because of the dominating inverse-square behavior. Evidence would, therefore, have to be looked
for near the peak of the spectrum. Several authors found deviations from a Thompson spectrum,
but a careful analysis by Szymonski & De Vries [169], who compared spectra for 6 keV Ar and
Xe bombardment on Ag and separated the linear portion from the measured spectrum, indicated
that, for Xe-Ag, thermal and linear sputtering contributed about equally to the measured yield.
The effect was found to be less pronounced for Xe-Au, presumably since gold has a higher
sublimation energy (3.8 vs. 3.1 eV).

While one may question whether it is justified to express a high local density of kinetic energy
in terms of a temperature, there is ample evidence in favor of the existence of such regions.
Figure 35 shows a crater formed by a 1 keV Ar ion in solid argon according to a molecular-
dynamics simulation by Urbassek & Waldeuer [170]. The three graphs refer to 3.2, 13.8 and 24.7
ps after the initial impact. Note that the bulk binding energy in solid argon is 0.14 eV.

Figure 36 shows measured sputter yields of Ag and Au by Au\textsubscript{4} cluster bombardment. Yields
per incident atom reach up to 1560, and the highest sputter yield per incident cluster is $13 \times 1500 = 19,500$ atoms.

High energy density at low implant density is an attractive feature in applications such as
cluster-SIMS [171]. Cluster bombardment was even reported to generate fusion reactions [172],
although that ‘discovery’ had only a few months’ lifetime.
7.8. Electronic Sputtering

The first reports about sputtering by electronic processes referred to alkali halides bombarded with electrons well below 1 keV [175]. Atoms recoiling from electrons with so low an energy are not able to overcome the surface binding energy. While one might argue whether this phenomenon – which cannot be explained in terms of kinetic energy transferred from an impinging particle to a target atom – should sort under the heading of atomic collisions, it has become customary to associate the term sputtering with any process that generates recoil atoms with energies in the few-eV energy range. Examples are laser sputtering, potential sputtering (to be mentioned below) and electronic sputtering by light and heavy ions.

Sputtering from alkali halides and other ionic crystals was considered as a rather special phenomenon, until Brown et al. [173] reported sputtering of water ice by H, He and C ions at MeV energies with sputter yields up to two orders of magnitude above what could be expected from nuclear sputtering (figure 37). Remarkably, the variation with the atomic number of the ion was significantly steeper than the \(Z_i^2\) dependence which one could have expected from the electronic stopping cross section. At the same time, the observed sputter yield for 1.5 MeV protons, 0.2 molecules per incident ion, was indicative of a linear process, whereas a yield of 640 molecules per ion for \(^{12}\)C suggested a nonlinear process.

Figure 38 shows the dependence of the sputter yield on the beam energy for several ions. While this may be taken as a convincing demonstration of the presence of both nuclear and electronic sputtering, the lines drawn through the points should not be understand as sums of nuclear and electronic energy losses, since the conversion factors from deposited energy to sputter yields may
TABLE I. Measured and calculated erosion or sputtering of the film thickness uniformity. Not only does the film grow thinner than average in some regions, the process can be controlled through various mechanisms.

## Figure 37: Sputter yields of 1.5 Mev H, He, $^{12}$C and $^{16}$C ions from water ice. From [173].

Differ significantly.

Whereas sputtering by elastic or quasi-elastic collisions is a universal process, electronic sputtering has gradually turned out to be very material dependent. The phenomenon has been observed mostly on insulators, with the exception of a small number of refractory metals [176], in agreement with earlier observations on damage tracks [177]. Consequently, studying electronic sputtering is as much a branch of materials science as of atomic-collision physics.

Sputtering effects on organic films bombarded by fission fragments were observed in 1976 [10], explored in the nuclear- and electronic-stopping regime and applied as a tool in mass spectrometry of large molecules [179].

Figures 27, 31, 36 and 38 have in common that the sputter yield approaches an apparent or real threshold with decreasing beam energy. Figure 39 shows that this is not a universal feature.
In analogy to a well-known phenomenon in secondary electron emission [180] this phenomenon is called potential sputtering. The roots of this field appear to lie in Tashkent and have been reviewed by Parilis et al. [181]. The first measurements date were followed up by a model involving Coulomb explosion [182]. The work reported in ref. [178], focusing on very low beam energies, stimulated systematic experimental studies on several materials as well as theoretical models [183]. Interaction of highly charged ions with material surfaces is still a very active area, but not being an expert I prefer to refer to Aumayr and Winter [184] for an illuminating review.
8. Concluding Remarks

A number of major topical areas have been more or less ignored in this essay, amongst which I like to mention elastic and inelastic collisions at surfaces, especially neutralization and ionization and studies at grazing incidence, radiation phenomena in multicomponent targets, especially ion-beam mixing, alloy sputtering and segregation and, moreover, tracks of charged particles, ion-induced electron and ion emission, ion-induced surface topography and sputtering of clusters. Nevertheless, some general trends can be identified which characterize the entire field of atomic collisions in solids.

First of all, over the entire period covered there has been a tight connection between theory and experiment. With a small number of theoreticians and a large number of experimentalists, theorists are rarely left on their own to consider problems that are not directly related to measurable quantities and the interpretation of experimental findings. With the development in computing, an increasing number of experimentalists have become engaged in simulational work which can replace traditional theory where fundamental equations are available.

Another characteristic feature is the tight connection between basic and applied research. It took less than five years from the discovery of channeling until the phenomenon played a central role in the development of electronic devices, and already in 1972 the first pocket calculator containing an ion-implanted chip, the HP-35, came on the market. Conversely, the development of Rutherford backscattering as a tool in surface analysis as well as lattice location of implanted ions was very much stimulated by the need for tools controlling the development and production of electronic devices.

I have mentioned a few controversies that occurred over the years. The fact that their number seems to decrease as time goes on may be a matter of maturity of the field, but also of increasing specialization. The conference photo of the first genuine ICACS conference, held in Chalk River, Canada in 1967, shows 102 individuals. With few notable exceptions this was the entire population of the field, and many of the participants were aware of what kind of research a sizable fraction of those people were engaged in, as well as some of their achievements.

On the other hand, despite the maturity of the field, significant discoveries have come up regularly. As examples I mention heating and cooling of channeled ions [40], formation of self-organized surface structures by ion bombardment [185] and ion guiding through capillaries in insulators [186].

Acknowledgements

The author’s contribution to this field of research has been, directly or indirectly, influenced by a large number of colleagues and students, amongst whom I wish to mention H. H. Andersen †, J. A. Davies †, L. G. Glazov, U. Haagerup †, J. Jensen, G. Leibfried †, J. Lindhard †, J. W. Mayer †, H. H. Mikkelsen, M. T. Robinson, A. Schinner, J. Schou, V. I. Shulga and K. B. Winterbon. This work has been supported by the Carlsberg Foundation.
