Charge-state fractions of hydrogen backscattered from gold

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Energy spectra of the three charge states and charge-state fractions of hydrogen and deuterium backscattered under ultrahigh-vacuum conditions from a polycrystalline clean gold surface are reported. The primary energy of the incident particles varies from 1 to 5 keV per atom. A comparison with measurements by different authors indicates a strong dependence of charge-state fractions on the cleanliness of the target material. No dependence on the primary energy of the impinging particles has been observed. The shape of the reported spectra indicates a high probability for destruction of negative ions near a solid surface.

I. INTRODUCTION

A large amount of both experimental and theoretical work on the backscattering of particles from a solid surface has been reported in the literature. However, very little quantitative data are available on the charge-state fractions of backscattered particles in the energy range below 5 keV primary incident energy. Theoretical investigations, e.g.,[1,2] are even more scarce, particularly for this energy region.

Nevertheless these data have significant practical applications. For example the backscattering of low-energy hydrogen atoms from metal surfaces has both technical and physical importance with regard to negative-ion sources[3] and plasma wall interaction problems in fusion devices.[4]

Buck *et al.* and Behrisch *et al.* have performed measurements on charge-state fractions of hydrogen backscattered from solid targets of Be, V, Cu, Nb, Mo, Ta,[5] and Au.[6] In these papers the negative charge state has not been taken into account, which can be justified at high energies ($\geqslant 20$ keV). Although most of their measurements have been performed at primary energies above 25 keV, the influence of adsorbate layers can clearly be seen, especially in the work of Buck *et al.* In the work of Behrisch *et al.* technical metals, where surface conditions are not known, have been used as targets. In both experiments the pressure in the vacuum system ($> 2 \times 10^{-8}$ Torr) was not sufficiently low to allow measurements on really clean surfaces. Only small differences were found in the charged fraction for different materials, which suggests adsorbed layers of residual gases and oxide layers were present on the surfaces. These may greatly influence the different charge states, especially for low-energy bombardment.

Measurements of charge-state fractions for ion bombardment of thin foils have been done at energies as low as 3 keV. Phillips[7] reported charge

equilibrium ratios for hydrogen after transmission through different foils. His experiment was performed under fairly poor vacuum conditions ($> 5 \times 10^{-6}$ Torr), and the results showed, that freshly coated foils (Al, Be, Ca, Ag, Au, SiO) exhibit a different behavior than those for which some time had elapsed after deposition. These differences have been accounted for both by adsorbing films of foreign material on the foils during the measurements, as well as by oxidation of the surface. But because of bad vacuum conditions, the initial conditions of the surfaces were not well characterized.

Berkner *et al.*[8] reported on measurements of charge-state fractions of deuterium beams emerging from thin foils of C, Mg, Nb, and Au, which have been freshly evaporated onto a carbon substrate, using a technique similar to Phillips's. These measurements have been performed at energies above 8 keV. Where the data overlap, the results are in agreement with the measurements of Phillips within the limits of error, although the vacuum conditions in the experiment of Berkner *et al.* were considerably better (10^{-8} Torr) than those of Phillips. In both the work of Phillips and Berkner *et al.* the thickness and composition of the adsorbate layers were not known.

In extension to earlier measurements where only charged particles could be detected[9] the aim of the experiment reported in this paper was to perform charge-state-fraction measurements for hydrogen backscattered from a more precisely defined surface under significantly better vacuum conditions. Gold was evaporated *in situ* onto a gold substrate under ultrahigh-vacuum-conditions. In addition it was possible to check the cleanliness of the surface *in situ* by low-energy Ne scattering (ion surface scattering) (also in Ref. 9) providing information on the kind and amount of adsorbed atoms. A second main purpose of this experiment was to extend charge-state-fraction measurements down to lower primary energies. A lower-energy limit

of detecting particles is determined by the method of measuring low-energy neutrals as will be explained later.

II. APPARATUS AND EXPERIMENTAL TECHNIQUE

The experiments have been performed with the Bombardon apparatus described elsewhere.[10] A mass-analyzed primary beam of hydrogen or deuterium ions impinges upon a solid-gold target. The beam from a duoplasmatron ion source with an energy spread of <25 eV was collimated by several diaphragms and had an angular divergence of 0.5° and a diameter of 0.5 mm at the target. The current density was typically 10 μA/cm^2 at 5 keV ion energy. At energies below 5 keV it was considerably lower.

The experimental setup is shown schematically in Fig. 1. The particles backscattered from the target consisted of positive and negative ions and neutral atoms. For measuring the ions, the "stripping chamber" was evacuated to a pressure below 1×10^{-6} Torr. Then by means of electrostatic deflection with a 90° cylindrical analyzer (energy resolution $E/\Delta E = 20$) the desired charged state was separated from the rest of the beam, energy analyzed, and then detected by a channel electron multiplier (CEM). The entrance of this CEM was kept at ground potential, so that both negative and positive ions impinged with their original energy. The particles not analyzed could leave the electrostatic analyzer through openings that were explicitly provided for this purpose, thus not

interfering with the charge state being analyzed at a time. For analyzing the neutral charge state a field of 1000 V/cm, that removed the charged particles from the beam, was applied between the deflection plates. Simultaneously atoms in the metastable 2s state were quenched by this electric field, so that only ground-state atoms entered the stripping chamber, where a known fraction of the neutrals was ionized. This is important, since the stripping probability depends on the electronic state of the neutral atom. The stripping chamber had a length of 50 mm and was filled with 2×10^{-3}-Torr N$_2$. The stripped particles were energy analyzed in the same manner as was described for the charged backscattered particles. The solid angle of the neutral particle detection system was 7.6×10^{-6}.

The voltage applied to the cylindrical analyzer was raised in equal steps, that correspond to definite energy intervals, after a preset amount of charge had impinged on the target within the specified energy interval.

The calibration of the stripping chamber[11] was performed in a separate setup. A neutral hydrogen beam with well defined energy entered the neutral particle detection system (see Fig. 1), where the stripped particles and the remaining neutral particles were detected simultaneously with nearly identical CEMs. The stripping chamber efficiency, determined as the ratio of both counting rates assuming equal detection efficiencies of the CEMs for positive and neutral atoms at the same energy, was measured down to 150 eV, with a maximum error of 100% at this energy.

By using a CEM, even very low currents of backscattered particles could be measured. For the detection efficiency of the CEMs the curves for H$^+$ and H$^-$ of Crandall $et\,al.$[12] have been used for energies above 300 eV. For lower energies the detection efficiencies have been determined by measurements in the same apparatus as used for the calibration of the stripping chamber.[13]

The target consisted of a 15-mm-diam disk of polycrystalline gold with a mean roughness of 0.1 μm after mechanical polishing. It was mounted on a goniometer head. The target was heated to 950 °C $in\,situ$, but this did not result in an atomically clean surface as was seen by low-energy Ne scattering (ion surface scattering). These Ne spectra were taken in the scattering chamber by means of a spherical condenser with an energy resolution of $E/\Delta E = 140$. Clean (99.98) fresh material could also be evaporated onto the substrate $in\,situ$ while the target chamber was maintained at UHV. To accomplish this an Au wire was vaporized in a tungsten spiral. These freshly produced surface layers had a considerably reduced
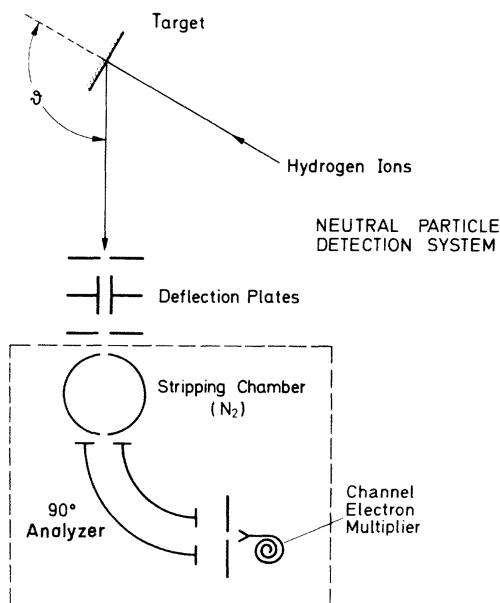

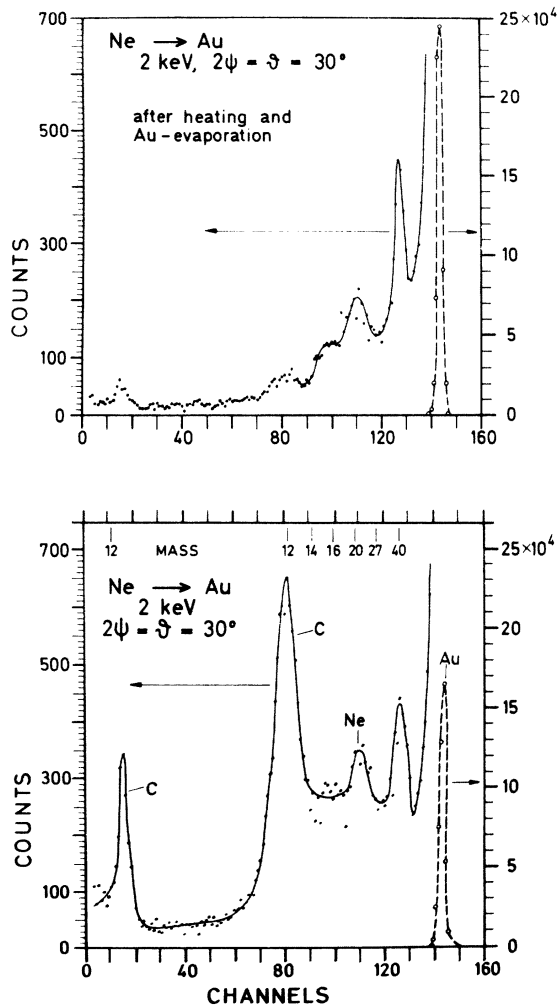FIG. 1. Schematic of the experimental setup.

FIG. 2. Backscattering spectra of 2-keV Ne ions at $\vartheta = 135°$ before and after Au evaporation onto the Au substrate. ψ is the angle of the incident beam relative to the surface.

surface contamination. Figure 2 shows ISS plots before and after evaporation. Mass 40 is probably a bulk impurity. An estimate of the amount of adsorbed species after evaporation of Au onto the substrate, taking into account scattering and neutralization cross sections, gives a value of about a hundredth of a monolayer. X-ray diffraction measurements showed that the Au target recrystallized by the heat treatment, creating grains of ≈ 0.1 mm diameter with a preferred orientation with twofold symmetry at the surface [(110) surface].

The scattering chamber is an UHV system pumped with ion pumps (1000 liter/sec) and a large Ti-sublimation pump (20 000 liter/sec for hydrogen with cooling by liquid N_2). The chamber was baked at a temperature of 150 °C for 12 h. After that treatment the typical pressure inside
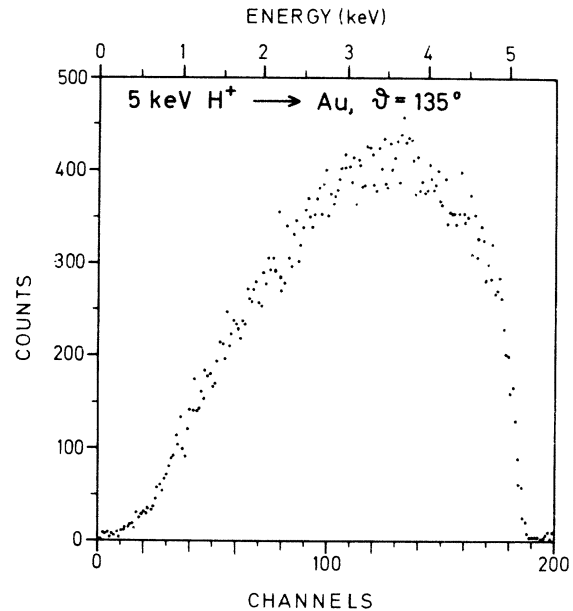

FIG. 3. Measured energy spectrum of neutral hydrogen backscattered at $\vartheta = 135°$ from an Au target bombarded with 5 keV protons.

the system was 2×10^{-10} Torr without gas, and 4×10^{-9} Torr with gas in the stripping cell.

The neutral particle detection system was attached to the scattering chamber from the outside. It was pumped with a turbomolecular pump (480 liter/sec); the pressure was two orders of magnitude higher than in the scattering chamber.

III. DATA PROCESSING

A computer plot of the energy spectrum of backscattered neutrals as measured at $\vartheta = 135°$ for 5 keV primary protons is shown in Fig. 3. The en-
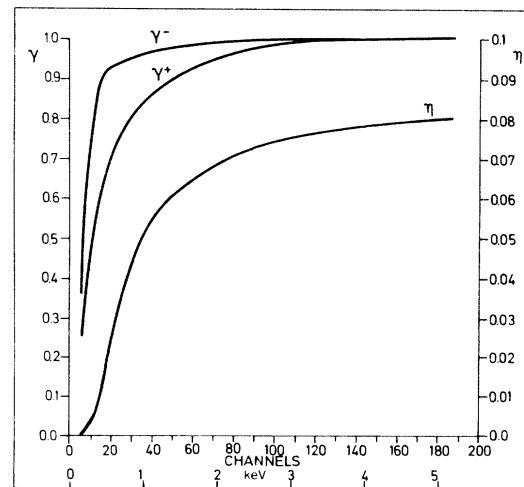

FIG. 4. Calibration curve of the neutral particle analyzer η and the channeltron efficiencies γ^+ and γ^- for hydrogen (for explanation see text).
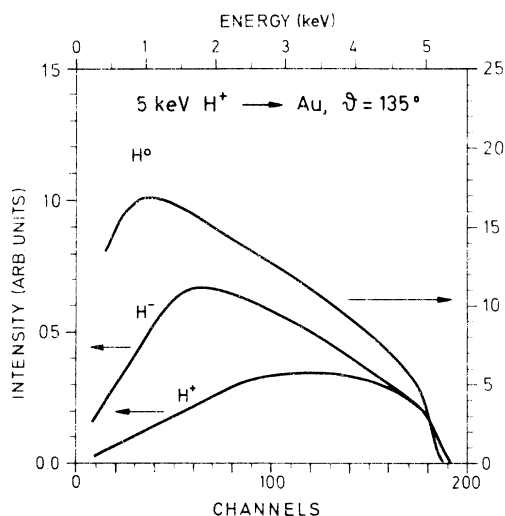
FIG. 5. Energy spectra of the three charge-state frac-
tions backscattered at $\vartheta = 135°$ from polycrystalline Au
bombarded with 5 keV H$^+$.

FIG. 6. Energy spectra of all particles backscattered
at $\vartheta = 135°$ from polycrystalline Au bombarded with H$^+$,
H$_2^+$, and H$_3^+$ of different energies.

ergy spectra of the ions have a similar shape.
The same is true for different primary energies.
These spectra must be normalized to equal num-
ber of primary atoms per channel and per spec-
trum. Since $E/\Delta E$ is constant for the cylindrical
condenser, these spectra have to be corrected so
that each channel corresponds to the same energy
interval ΔE. Furthermore, the energy dependence
of the detection efficiencies of the CEM (see Fig.
4 for hydrogen) must be taken into account, γ^-
for the spectra of negative particles, γ^+ for the
positive and neutral particle spectra. Addition-
ally, the neutral spectra have to be divided by the
calibration curve η of the stripping chamber.

Analogous correction curves were applied for
deuterium scattering. The efficiency curves for
D$^+$ and D$^-$ were derived from the hydrogen curves,
reducing the energy scale by a factor of 2, so that
H and D are compared at the same velocity.[14]

IV. RESULTS

All measurements of charge-state fractions were
performed for normal incidence and at a scatter-
ing angle $\vartheta = 135°$, i.e., at an angle of emergence
of 45° relative to the surface. The energy spectra
of the three backscattered charge states for a pri-
mary beam of 5 keV protons are shown in Fig. 5.
The spectrum of the negatively backscattered par-
ticles is quite different in shape from the spec-
trum of the positive particles. The number of neg-
ative backscattered ions exceeds the number of
positive ions in the energy range considered, as
has been found earlier.[13] There are about twice
as many negative particles backscattered than
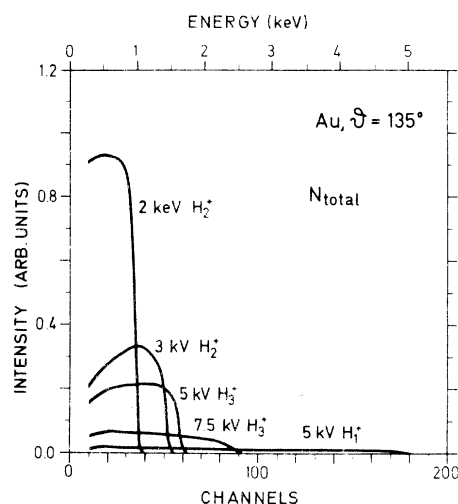positive particles.

The negative ion yield exhibits a distinctive
maximum at 1.7 keV, whereas for the positive
particles there is a flat energy distribution. The
spectrum of the total number of backscattered par-
ticles $N_{tot} = N^0 + N^+ + N^-$ is only slightly different
from the spectrum of the neutrals, since the frac-
tion of charged particles is less than 10% at all
energies considered here.

Plots of total backscattering spectra for hydro-
gen and deuterium are given in Figs. 6 and 7 for
different primary energies. As is evident from
these figures, backscattered deuterium has a
more pronounced maximum in the energy distri-
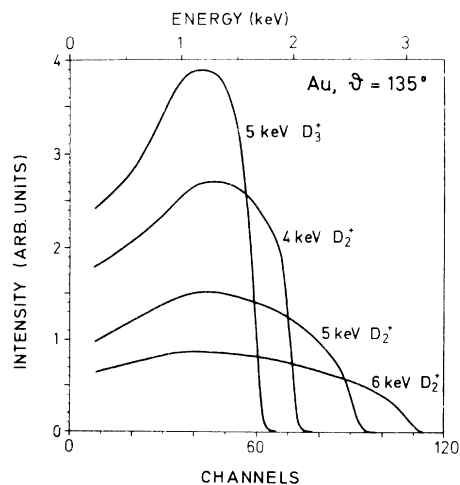bution. As can also be seen, backscattering spec-

FIG. 7. Energy spectra of all particles backscattered
at $\vartheta = 135°$ from polycrystalline Au bombarded with D_2^+
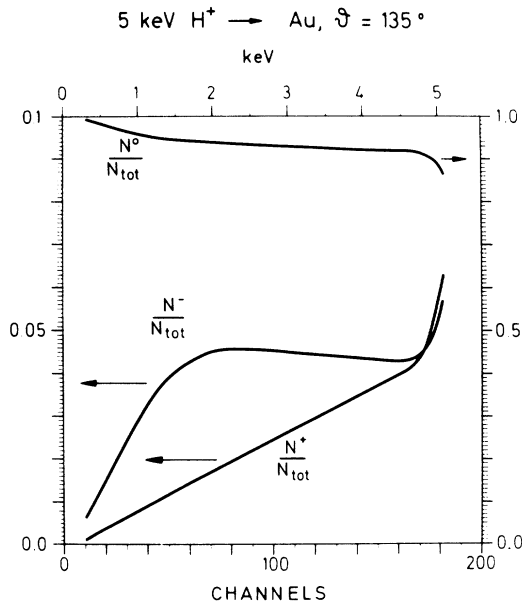and D_3^+ of different energies.

FIG. 8. Three charge-state fractions as a function of energy backscattered at $\vartheta = 135°$ from polycrystalline Au bombarded with 5 keV H^+.

FIG. 9. Ratio of negative particles to positive particles N^-/N^+ as a function of energy for polycrystalline Au bombarded with 5 keV D_3^+ for different scattering angles ϑ. ψ is the angle of the incident beam relative to the surface.

tra for high primary energy are of more trapezoidal shape, whereas for low energy, e.g., 5 keV D_3^+, which is equivalent to 1.6 keV D^+, a sharp maximum occurs.

Charge-state fractions for the spectra shown in Fig. 5 are given in Fig. 8. The fraction of the positive particles N^+/N_{tot} is linearly increasing with energy, whereas the fraction of negative particles N^-/N_{tot} has a maximum value of $\approx 4.5\%$ at 2.3 keV.

In Fig. 9 the energy dependence of N^-/N^+ is shown for 5 keV D_3^+ primary ions for different scattering angles ϑ. These curves have been measured with the same spherical condenser ($E/\Delta E = 140$) used for the Ne scattering. In contrast to the results reported above and to earlier measurements[13] the scattering angle has been varied. There is a strong dependence of the ratio N^-/N^+ on the scattering angle.

It should be mentioned that the energy spectrum of the neutrals depends critically on the calibration curve of the neutral particle analyzer. Thus a constant background, taking into account the calibration curve of the neutral particle analyzer, would result in an extremely high increase of the neutral backscattering yield at low energies, where the stripping efficiency is extremely small. This effect is enhanced by including the channeltron efficiencies, which also become very small at low energies. The uncertainty at the lower end of the stripping efficiency curves is due to the difficulties of the calibration procedure.
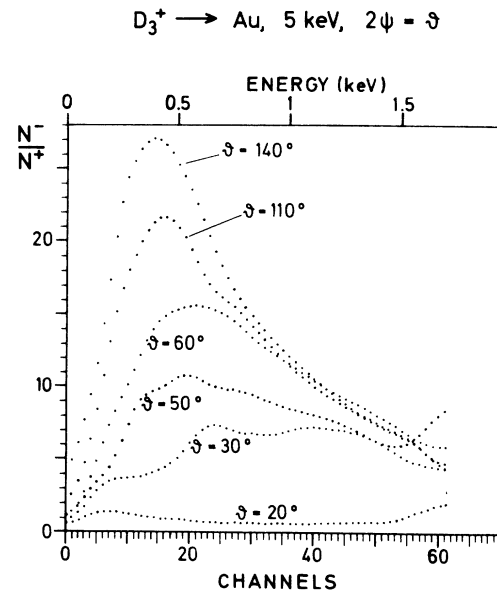
V. DISCUSSION

Theoretical calculations on charge-state fractions of hydrogen atoms after leaving a solid surface have been performed by different authors.[2,15,16] Zaidins[1] has calculated charged fractions on an empirical statistical basis. These calculations are in nearly quantitative agreement for the negative ions as measured in this work, whereas for the positive charge state his values are higher by a factor of more than 3. These calculations, however, give no information on the physical processes involved.

Yavlinskii et al.[2] calculated charged fractions by treating the electron pick up by a proton that takes place at a metal surface as a recombination process. This calculation gives expressions for the fraction N^+/N^0, depending on the velocity v_p of the proton relative to the speed v_0 of an electron at the Fermi surface. For $v_p \ll v_0$, which is the region of the measurements performed in this paper, the following expression holds:

$$N^+/N_{tot} = \exp\left[-(136/E_p)^{1/2}(n_0/10^{22})^{1/6}\right],$$

where n_0 is the conduction electron density within the metal and E_p the proton energy.

Values from these formulas deviate significantly from the curves reported in this paper and also from curves in earlier work.[5] Both the shape of the curves and the magnitudes of the values disagree. In a later paper,[16] Trubnikov and Yavlinskii included the case of tunnel recombination in
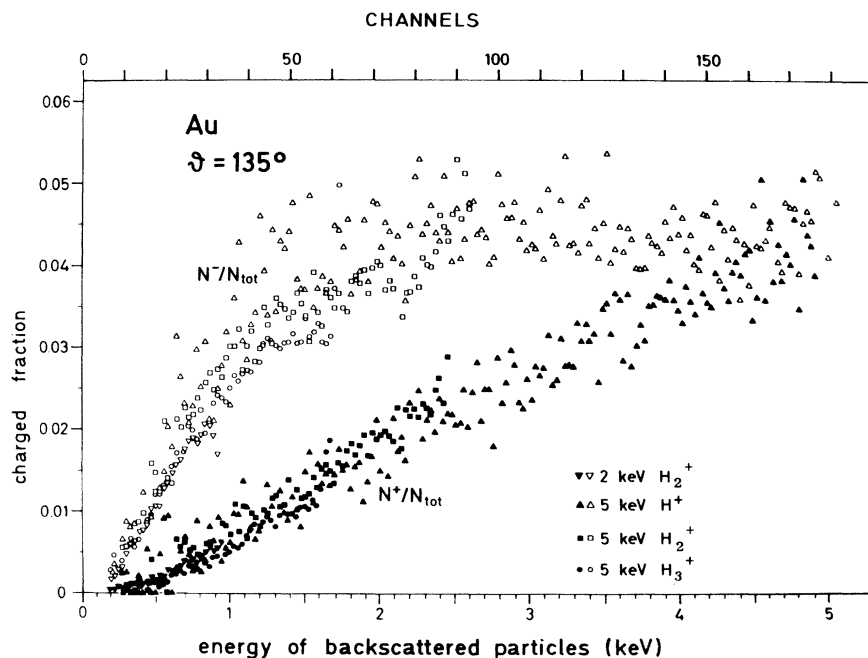
CHANNELS

FIG. 10. Charged frac-
tions of particles backscat-
tered at $\vartheta = 135°$ from poly-
crystalline Au bombarded
with H^+, H_2^+, and H_3^+ of
different energies.

their considerations. Both processes can take
place in principle, but the large deviations from
the experimental values indicate that other mech-
anisms must contribute to the capture process.

Other theoretical treatments,[15] that deal with the
recombination of ions at metal surfaces do either
apply to a completely different energy region, or
fail to come close to experimental findings.

Therefore in this paper the authors do not intend
to present a model that explains experimental
charge-state fractions, but rather give some more
qualitative conclusions which can be drawn from
the experiments reported here.

No dependence of charge-state fractions on the
primary particle energy or penetration depth has
been observed (Fig. 10). This is not in disagree-
ment with the theoretical considerations of
Brandt,[17] according to which the projectile inside
the metal moves as a bare ion. The data indicate
that the charge-state fraction is determined in a
thin region near the surface, possibly as the par-
ticle leaves the surface. The length of this region
must be short compared to a measurable quantity
of energy loss. Within the limits of error, the
charge-state fractions do not depend on the energy
of the particles but on the velocity or energy per
nucleon, which can be seen when comparing hydro-
gen and deuterium (Fig. 11).

The maximum value of 4.5% for the negative
charge-state fraction is surprisingly high, espec-
ially if the assumption of a two-step process is
made. For this assumption the ratio $(N^0+N^-)/N_{tot}$
$\approx N^0/N_{tot}$ would give the neutralization probability

of an impinging ion and $N^-/(N^0+N^-) \approx N^-/N_{tot}$ the
probability of formation of negative ions from
neutral atoms, which may be partly in an excited
metastable state.

Since the cross section for electron capture may
be an order of magnitude higher for some excited
states than for the ground state,[18] $N^-/(N^0+N^-)$ is
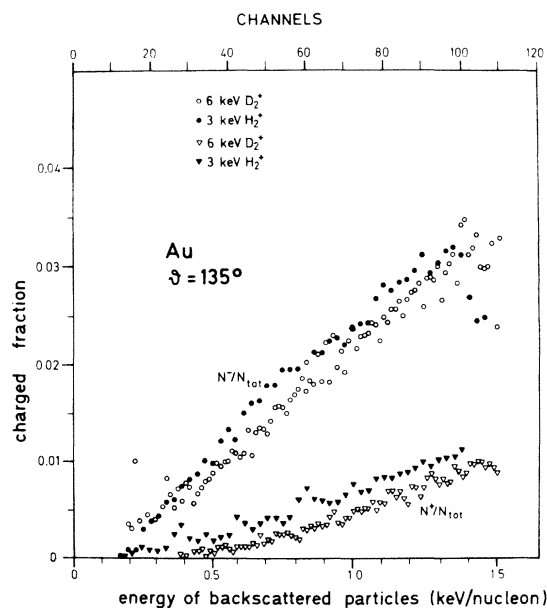also a maximum value for the ratio of backscat-

CHANNELS

FIG. 11. Charged fractions of particles backscattered
at $\vartheta = 135°$ from polycrystalline Au bombarded with D_2^+
and H_2^+ of the same energy per nucleon.

tered excited atoms to ground-state atoms. From the work of Berkner *et al.*[8] a value of 0.1 for that ratio may be concluded. Gas-phase measurements[18] show that the cross section for the destruction of a metastable state is in certain cases governed by electron capture rather than electron loss or radiative de-excitation. At a metal surface with a high density of quasi-free-electrons the electron-capture process seems to be dominant. On the other hand it is quite obvious from this idea that the neutral charge-state fraction and particularly the negative charge-state fraction should decrease with increasing energy. The experiment reported in this paper, however, leads to an increasing negative fraction for energies below 2.3 keV. Above 2.3 keV it takes an almost constant value of 4.5%. Therefore at least another different process must contribute to negative ion formation.

A quantum-mechanical treatment by Janev[19] shows that there is also a high probability for resonant destruction of a negative ion near a solid surface due to electron tunneling. This effect is particularly important at the low-energy side of the spectrum reported in this paper and might explain the behavior of the N^-/N_{tot} curve, especially the maximum, together with effects mentioned above.

This high probability of destruction of negative ions is further supported by measurements of N^-/N^+ (Fig. 9) at different angles of emergence.

(See also Ref. 20.) The ratio N^-/N^+ is decreasing with more grazing angles of emergence, i.e., when the negative ion is close to the surface for a longer time, the probability of destruction is higher.

Comparisons with results by other authors and earlier measurements are difficult to make, because the energy regions do not coincide. A comparison of the measurements reported here with measurements by Behrisch *et al.*[5] and Meischner and Verbeek,[21] which were performed on more or less practical surfaces, shows that for a clean Au surface the positive charge-state fraction is smaller by a factor of up to 10 than for a practical surface, where adsorbate layers change the electronic structure of the surface quite drastically.

In this paper measurements on a clean surface have been reported. The explicit dependence of charge-state fractions on the coverage of the surface with adsorbate layers remains open for further investigation.

ACKNOWLEDGMENTS

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