Transmission of 3 keV Ne^{7+} Ions through Nanocapillaries Etched in Polymer Foils: Evidence for Capillary Guiding

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We report unprecedented transmission experiments of 3 keV Ne^{7+} ions through capillaries of 100 nm diameter and 10 μm length produced by etching ion tracks in a polymer foil. We studied foils tilted up to ±20° for which the incident ions are forced to interact with the capillary surface. Surprisingly, the majority of Ne^{7+} ions were found to survive the surface scattering events in their initial charge state. The angular distributions of the transmitted particles indicate propagation of the Ne^{7+} ions along the capillary axis. This *capillary guiding* of the Ne^{7+} ion provides evidence that the inner walls of the capillaries become charged and electron capture from the surface is suppressed in a self-organizing process.

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In the past few years considerable work has been devoted to studies of nanostructures produced at surfaces and in solids. This effort has been initiated by the continuous need for refining the miniaturization of interfaces used in microelectronics and related fields. Particular attention has been paid to linear structures of mesoscopic dimensions, such as pores or capillaries [1]. Advantageous tools for producing capillaries with great precision are ion tracks created by energetic projectiles in the solid [2]. Using well-known etching techniques, the ion tracks can be transformed to capillaries with mesoscopic dimensions ranging from a few nm to a few μm [3]. Since it is difficult to study the interior of tiny tubes, there is an obvious need for methods that probe the physical and chemical properties of the capillary surface.

Capillaries in an Al_2O_3 insulator were studied using slow highly charged ions by Yamazaki *et al.* [4] who avoided charge-up effects by means of an additional beam of slow electrons. Later capillary work [5] was focused on metallic materials whose surface properties are well known [6,7]. For metals it is commonly accepted that multiply charged ions capture several electrons in high lying states leaving the inner shells empty so that *hollow atoms* are produced [8,9]. These atoms undergo Auger processes which sequentially deexcite the electronic states to fill the inner shells of the hollow atoms [10,11]. Charge exchange processes may occur upon exit from the solid so that the decay of hollow atoms can be observed outside the capillaries [5,12].

In the present work, we study the transmission of Ne^{7+} ions through capillaries formed by etching ion tracks in polymers [13]. The measurements were focused on the angular distributions of Ne^{7+} ions transmitted through capillaries of 100 nm diameter in a highly insulating foil of polyethylene terephthalate (PET or Mylar). The angular distributions provide clear evidence that the Ne^{7+} ions are guided within the capillaries. This mesoscopic *capillary guiding* is remarkable for highly charged ions, since it involves multiple scattering events at the surface while preserving the incident charge state. This unexpected observation is attributed to self-organizing charge-up effects that inhibit close contact with the capillary walls.

The experiments were performed at the 14.5 GHz Electron Cyclotron Resonance (ECR) source at the Ionenstrahl-Labor of the Hahn-Meitner-Institut Berlin. The PET foil of 10 μm thickness was previously irradiated by 1 GeV xenon ions at the Flerov Institute in Dubna [14]. Using NaOH for chemical etching of the ion tracks we produced capillaries with a diameter of 100 nm. To avoid charge up of the front and back sides of the PET foil, Au films of ~30 nm thickness were evaporated under 45° on both sides. Atomic force microscopy was used to verify that the openings of the capillaries are nearly circular and cover a surface fraction of ~4%. Scanning electron microscopy was utilized to study the edge of a newly cut PET foil which showed that the diameter of the capillaries remains constant inside the solid.

The PET foil was positioned at a goniometer in a UHV chamber [11,15] operated at a pressure of a some 10^{-10} mbar. A Ne^{7+} ion beam from the ECR source was collimated to a diameter of 1.5 mm and a divergence of about 0.5°. The transmitted neon ions were measured with an energy resolution of 5% by means of an electrostatic analyzer [11,15]. We also measured neutralized neon atoms that passed through a hole in the backplate of the electrostatic analyzer. The spectrometer acceptance angle was 0.8° (FWHM). A measurement of the primary ion beam (without PET foil) yielded a rather narrow angular distribution of 1° FWHM due to the folding of the angular acceptance over the beam divergence.

Figure 1 shows typical ion spectra obtained with PET foils tilted by the angles of $\psi = 0°$ and 5°. These spectra were acquired at an observation angle equal to the tilt angle, $\theta = \psi$, whereas data shown below were also taken with $\theta \neq \psi$. As shown in the inset, the observation angle is defined with respect to the incident beam direction. Interestingly, for 0°, the PET charge-state spectra are similar to those obtained for Ag capillaries also prepared in this work and the Ni capillaries studied previously [5]. It is

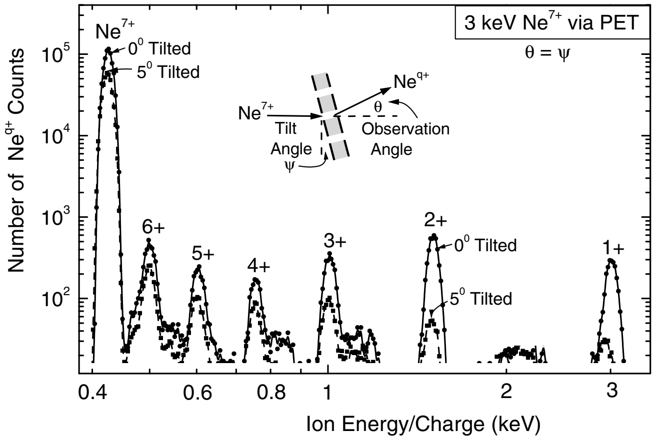

FIG. 1. Charge state spectra of Ne^{q+} ions produced after the passage of Ne^{7+} through capillaries in PET. The charge state q is given at each peak. The tilt angles are $\psi = 0°$ and 5° as indicated at the spectra. The ion observation angle is $\theta = \psi$. The angles are defined by means of the diagram shown as an inset in the figure.

seen that the intensity of the transmitted ions with charge state 7 is dominant, whereas the intensities of the other charge states, including neutrals, are much smaller. In the following, the attention is focused on the surprising results for the dominant charge state 7.

In Fig. 2 the integrated peak intensity of the transmitted Ne^{7+} ions is plotted as a function of the observation angle θ. The data were acquired for different tilt angles ψ varying from $-20°$ to 20° in steps of 5°. At a 0° tilt angle we estimated the significant amount of ~50% for the Ne^{7+} transmission; i.e., the number transmitted ions relative to those entering into the capillary. The PET data are compared with results obtained with capillaries covered by Ag. The angular distributions for the two cases are found to be entirely different. For Ag capillaries, the angular distribution is peaked at 0° with a rather narrow width of 1.2° (FWHM). A similar result is obtained for the Ag capillaries, when the foil is tilted by 5°.

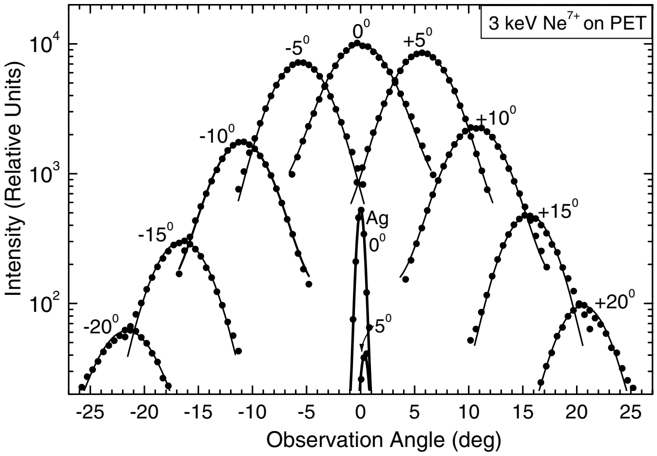

FIG. 2. Angular distribution of Ne^{7+} ions transmitted through capillaries in PET. The foils were tilted by the angles as indicated in the figure. The solid lines represent Gaussian functions fitted to the data. The distinct peaks near 0° were obtained using capillaries covered with Ag.

On the contrary, the angular distributions for the Ne^{7+} ions transmitted through the capillaries in PET are seen to be rather broad with a width of ~5° (FWHM), which is nearly independent of the tilt angle (Fig. 2). For smaller charge states of the projectile, similar distributions were observed with decreasing angular width (e.g., ~2° FWHM for Ne^{+}). The most important finding is that for the tilted foils the centroids of the angular distributions are significantly shifted with respect to the 0° data. In fact, each centroid angle nearly coincides with the related tilt angle. For instance, when the foil is tilted by ±5° the centroid of the corresponding angular distribution is observed close to ±5°. The angular distributions for pairs of angles $-\theta$ and θ are found to be equal within the experimental uncertainties.

The shifts of the angular distributions indicate that the direction of the incident Ne^{7+} ions is altered to a preferential direction parallel to the capillary axis. It should be realized that with the present capillary aspect ratio of 100 (10 μm length versus 0.1 μm diameter) the maximum angle is ~0.5° for ions traveling on a straight line without touching the inner wall of the capillary (see also the Ag data). Consequently, Ne^{7+} ions transmitted through foils tilted with angles ≥5° have to interact at least once with the inner wall of the capillary. This finding is remarkable, since it is well known from previous studies [16,17] that highly charged ions are practically all neutralized when scattered by angles of a few degrees at the surface. Thus, for the tilted foils the intensity of transmitted Ne^{7+} ions should be virtually zero. However, as seen in Fig. 2 , the intensity loss is minor for Ne^{7+} ions transmitted through capillaries with the 5° tilt angle and the Ne^{7+} intensity is still significant at tilt angles as large as 20°. This shows that additional effects must be considered to solve the inconsistency with the neutralization probabilities commonly accepted [16,17].

The additional effects are likely to be associated with electric fields in the capillaries. The enhanced ion transmission suggests that the inner walls of the capillaries collect charges so that electrostatic repulsion inhibits close collisions with the surface and, in turn, electron capture to the projectile. To support this picture it is noted that with a beam of 1.3 nA Ne^{7+} the number of $J_{\text{in}} \approx 2200$ elementary charges per minute enter into a single capillary. This number suggests significant charge-up effects which may enhance the capillary transmission.

The change of the capillary transmission was verified experimentally as shown in Fig. 3. First, a beam of 1.3 nA Ne^{7+} ions was directed onto the PET foil tilted at 10°. The ion detector was set to a fixed deflection voltage to observe the transmitted Ne^{7+} ions at 10°, i.e., at the maximum of the angular distribution. However, just after the beam is turned on, the Ne^{7+} intensity is very small and it becomes significant only after a few minutes. After 10 min, the Ne^{7+} intensity has reached equilibrium. Then,

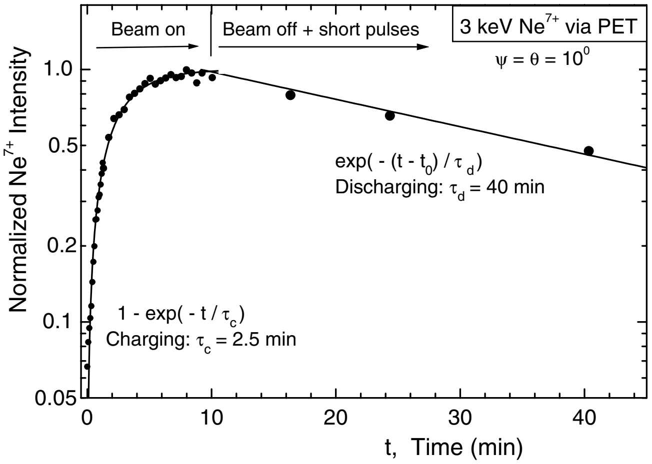

FIG. 3. Time dependence of the transmitted Ne^{7+} intensity showing the charging and discharging phenomena of capillaries in PET. A beam of 1.3 nA Ne^{7+} ions is directed onto the PET foil tilted at 10°. The transmitted Ne^{7+} intensity, measured at 10°, increases exponentially with a time constant of 2.5 min. After 10 min the beam is turned off. Short beam pulses probe the decrease of the transmission with a time constant of 40 min (see text).

the beam was turned off and the transmission of the capillaries started to decrease, as probed by using short beam pulses. In fact, an enhanced capillary transmission was still measurable after several hours. This large time constant is important for the present experiments. It implies that the capillary transmission remains stable over a significant time period, which allowed angular distribution measurements in a reproducible manner.

To describe the time dependence of the transmitted Ne^{7+} intensity, we introduce the scenario shown in Fig. 4. It is important to note that the incident ions deposit positive charges on the capillary surface in a self-organizing manner, which involves charge accumulation until the ions are deflected by electrostatic repulsion which, in turn, limits further charge collection. Although we expect that the self-supporting charge deposition causes the ion transmission through the capillary, the details of the guiding process are not fully understood at present.

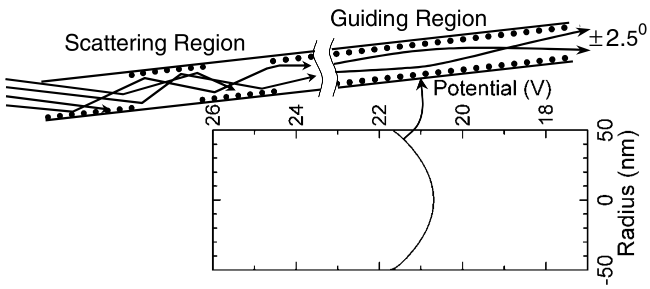

FIG. 4. Guiding of highly charged ions in a PET capillary. The graph shows results of the calculated potential inside the capillary. The influence of neighboring capillaries increases the absolute value of the potential by nearly a factor of 10, whereby the potential depth is unchanged.

For a preliminary analysis consider two sections, referred to as scattering and guiding regions (Fig. 4). The distinction of the two regions is supported by the finding of the same angular width of ~5° (FWHM) for all tilt angles (Fig. 2) suggesting that the processes occurring in the scattering region are independent of those in the guiding region. In the first region, the ions are deflected from one side of the capillary to the other. The deflection implies angular straggling (enhanced by the surface roughness) and, hence, after a few scattering events, the ions will loose their memory of the incident (tilt) direction. Then, in the second region, the ions are guided until the end of the capillary.

One might consider that the guiding region does not exist, i.e., that the scattering region extends till the end of the capillary. In this case, however, the transmitted ions may have an asymmetric angular distribution which was not found in the experiments. Rather, symmetric distributions of constant width were observed (Fig. 2) suggesting that the ion beam is guided with a divergence of about ±2.5°. Note that a 3 keV particle with this divergence, has a rather small transverse energy of 5 eV. With charge state 7 such a particle will be guided in a potential with a depth of $\gtrsim 0.8$ V.

The capillary potential was estimated from the charge deposition using a simple model. The current $J_{\mathrm{in}} = J_a + J_p$ entering the capillary splits into the current J_a absorbed at the wall and J_p propagated through the capillary. Adopting a linear model, the propagated beam is assumed to be proportional to the charge Q deposited at the wall

$$J_p(t) = Q(t)/\tau_p\,, \qquad (1)$$

where τ_p is a time constant associated with the capillary charging. Similarly, assuming a constant conductivity of the PET one obtains for the discharge current

$$J_d(t) = Q(t)/\tau_d\,, \qquad (2)$$

where τ_d is the time constant due to the capillary discharging (Fig. 3). We realize that due to nonlinear effects, the discharge current may strongly be enhanced accounting for the observed reduction of the transmitted current with increasing tilt angle. The linear model is retained here since it is useful to estimate the charge deposited in the capillaries.

The change of the deposited charge is governed by the differential equation

$$\frac{dQ(t)}{dt} = J_a - J_d = J_{\mathrm{in}} - \left(\frac{1}{\tau_p} + \frac{1}{\tau_d}\right)Q(t)\,. \qquad (3)$$

The solution is obtained as $Q(t) = Q_\infty[1 - \exp(-t/\tau_c)]$, where $\tau_c = (1/\tau_p + 1/\tau_d)^{-1}$ is the time constant for the capillary charging and $Q_\infty = J_{\mathrm{in}}\tau_c$ is the final charge in the capillary. Using also Eq. (1) the transmitted Ne^{7+} intensity was fitted by the normalized function $1 - \exp(-t/\tau_c)$ yielding the time constant $\tau_c = 2.5$ min (Fig. 3). Similarly, after the beam is turned off after t_0 ($J_a = 0$), the transmission follows the exponential decay function $\exp[-(t - t_0)/\tau_d]$ with a time constant of $\tau_d = 40$ min.

Recalling that $J_{\rm in} = 2200e\ \mathrm{min}^{-1}$ and with $\tau_c = Q_\infty/J_{\rm in} = 2.5$ min one obtains $Q_\infty \approx 5500e$. With this equilibrium charge, the potential in the capillary was estimated. We note that with 5500 elementary charges uniformly distributed inside the capillary, the mean distance between two neighboring charges is about 25 nm. However, when the inner wall is uniformly covered with closely lying charges, the guiding diminishes due to the weakness of the electrostatic field in a capillary of large aspect ratio. (An infinite tube continuously charged is field free.) Consequently, the charge distribution is not uniform within the capillary. We made various attempts to verify nonuniform charge distributions providing a guiding field.

A suitable ion guiding is obtained when the charge deposition is kept constant along the capillary axis and varied with respect to the azimuthal angle of the capillary. This anisotropic charge deposition is plausible, since the ions are expected to keep some time their memory on the incident direction. Thus, the charge deposition in the incident plane associated with the azimuthal angles $\phi = 0$ and π is stronger than that in the perpendicular plane associated with $\phi = \pm\pi/2$. From a tentative $\cos^2\phi$ dependence of the charge deposition we obtain the focusing potential for the incident direction as shown in Fig. 4. The calculated potential exhibits a depth of ~1 V (Fig. 4). As pointed out above, this depth is sufficiently large for the 3 keV Ne^{7+} ions to be guided within the capillary. In particular, the shape of the potential allows for a guiding at a sufficiently large distance from the surface where charge exchange processes are diminished [6]. Thus, the surprisingly small probabilities for charge exchange may be understood.

Finally, we note that the present potential forms a saddle point involving a defocusing effect in the perpendicular ($\phi = \pm\pi/2$) direction. Thus, the $\cos^2\phi$ dependence is modified and new scenarios are expected. After preferential deposition of charge in the perpendicular plane, this charge may become as large as that deposited in the incident plane resulting in a quadrupole potential with focusing effects in all directions. Also, at the capillary exit a guiding field exists even for a uniform charge deposition. (Note that a finite capillary is not field free.)

In conclusion, we measured angular distributions of Ne^{7+} ions guided through nanocapillaries with a large aspect ratio. Our preliminary model indicates that the description of the capillary guiding is a challenging theoretical task that involves ordering phenomena by a self-organizing process. Furthermore, we expect that capillary guiding has considerable potential for obtaining information about the interaction of multiply charged ions with insulators, characterizing the inner walls of capillaries, and controlling the transport of highly charged ions within regions of mesoscopic dimensions. We plan further experiments to study in more detail the present results by varying the beam parameters, capillary dimensions, and materials.

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