

## Threshold effect in the energy loss of slow protons and deuterons channeled in Au crystals

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Measurements of the energy loss of protons and deuterons channeled in a very thin single-crystal foil of gold were performed, covering the range of very low velocities. The experimental results provide clear evidence of the deviation of the energy loss from the proportionality with ion velocity predicted theoretically, showing a transition between two well-defined regimes. We explain this behavior by a theoretical analysis that takes into account the electronic band structure properties of the medium, separating the contribution of the conduction band (described as a free Fermi gas) from the contribution of the nearly free *d* electrons of gold, which are affected by a threshold behavior due to the shift of the density of states of this band with respect to the Fermi level. The theoretical model yields a very good description of the experimental findings.

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It has been commonly accepted for many years, based on experimental evidence and theoretical expectations, that the energy loss of point particles in metals, in the range of low velocities, should be proportional to the ion velocity  $v$ . This behavior is theoretically predicted by linear as well as non-linear ion stopping models [1–4] for velocities in the range  $v < v_0$ , where  $v_0$  is Bohr's velocity.

However, more precise experimental studies of the energy loss of slow protons in thin polycrystalline metallic foils showed unexpected deviations from the proportionality with ion velocity for various transition metals in the range of very low energies (typically below 4 keV) [5]. The origin of these deviations has been interpreted as due to a threshold in the excitation of *d* electrons [5–7] which usually dominate the stopping process in transition metals at intermediate energies and whose band structure properties differ from those of free electrons.

The question of threshold effects in low-energy stopping coefficients has raised great interest recently, after a set of experimental studies with protons [8–10] and antiprotons [11] on high-band-gap insulators showed no evidence of the expected threshold effects. More recent measurements on LiF [12] did show a threshold, which appears at energies much smaller than the theoretical expectations for materials with similar band gaps [9].

The search for possible energy transfer thresholds in metals, as well as in insulators, is currently a subject of great interest and is also a question that requires deeper understanding, as it appears that some of the results confront the applicability of basic theoretical models used to describe the phenomena of electronic interactions and energy loss of slow particles in solids [11].

In this work we consider the problem of the energy loss of slow protons and deuterons channeled through very thin crystalline foils of gold. In particular, we aim to provide clear evidence of the effects of band structure on the stopping process for low-energy ions in transition metals, and to clarify its influence on the observed deviations from the velocity proportionality mentioned before.

For this purpose we made precise measurements of the energy loss of protons and deuterons in a very thin monocrystalline Au(100) target using the beam-foil transmission

method and with a narrow angular acceptance, of  $\pm 1^\circ$ , in the forward direction. Measurements in a monocrystal using the channeling technique lead to a sharp concentration of the emerging ions in the forward direction, allowing experiments down to smaller energies when measuring at  $0^\circ$ .

Additionally, in order to further extend the explored range toward lower velocities we have used deuterons in addition to protons. By measuring with deuteron beams one gets a lower angular dispersion as compared with protons of the same velocity leading to higher transmitted signals. This method relies on the absence of isotopic effects on the energy loss, which has been proved previously for polycrystalline Au [13] and is verified in the present study for monocrystals.

The experimental setup has been described in previous publications [13]. The ion beams were generated in an electrostatic accelerator with a hot discharge ion source with small energy dispersion, followed by a Wien filter for mass selection and electrostatic bending for elimination of neutrals. The ions emerging in the forward direction from the monocrystalline Au (100)-oriented foil were energy analyzed by an electrostatic spectrometer of 3% resolution and subsequently detected by an electron multiplier followed by standard pulse-processing electronics and a multichannel scaler. With this setup the energy loss values are determined with a precision of  $\pm 5$  eV.

Monocrystalline gold targets (mounted on a 3 mm transmission electron microscope grid) were obtained from Pelco International [14]. The nominal thickness of the foil used in these experiments was 11 nm, and evaluation by means of energy loss measurements and normalization to the Au (100) stopping values of Ref. [15] at 6.6 keV yielded 12 nm.

No foil thickening by ion beam bombardment was observed within the precision of the experiments, by repeating the measurements at the same initial energies after each of the experimental runs. The total beam fluency was lower than  $2 \times 10^{13}$  ions/cm<sup>2</sup>.

The energy loss spectra showed a nearly Gaussian shape, which allowed a precise determination of the mean energy loss. In Fig. 1 we show the energy loss data for protons and deuterons as a function of the average velocity  $\langle v \rangle$  of the ions in the foil [ $\langle v \rangle = \frac{1}{2}(v_{\text{in}} + v_{\text{out}})$ ], covering the velocity range

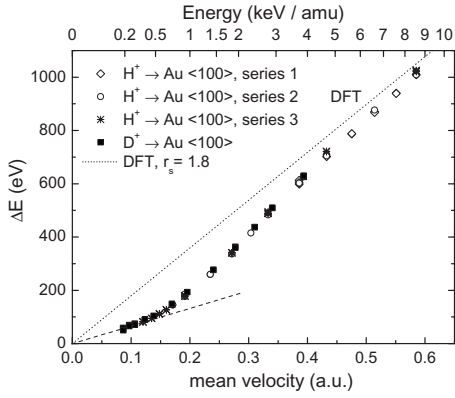


FIG. 1. Energy loss of protons and deuterons channeled through a 12 nm monocrystalline gold foil oriented along the  $\langle 100 \rangle$  direction, as a function of the mean projectile velocity (with equivalent energy shown on the upper scale). The data of different series of measurements are displayed with different symbols, showing the low experimental dispersion and the excellent coincidence of the proton and deuteron results, indicating the absence of isotopic effects. The dotted line shows calculations according to the DFT for a free-electron gas with  $r_s=1.8$ ; the dashed line is a visual guide for the low-velocity behavior.

from 0.086 to 0.58 a.u. (atomic units will be used in the following). The data of different series of measurements, displayed with different symbols, show the low experimental dispersion. The very good coincidence of the proton and deuteron results in the wide overlapping region ( $0.12 < \langle v \rangle < 0.4$ ) shows the absence of isotopic effects in the energy loss values within the limits of the experimental precision. For comparison, the theoretical values expected from density functional theory (DFT; see description below) are shown by a dotted line, corresponding to an  $r_s$  value of 1.8 for the Au $\langle 100 \rangle$  channel. Note that this  $r_s$  value is larger than the usual one for polycrystalline gold (1.5) due to the smaller electronic density found by the ion in the  $\langle 100 \rangle$  channel of Au [16]. The lower dashed line in this figure is only a visual guide. A remarkable feature observed here is the deviation from the expected linear velocity dependence, with a clear change in the slope around  $\langle v \rangle = 0.15$ . The region below this value shows an approximate proportionality with velocity with relatively low slope (much smaller than the one predicted by DFT), while at higher velocities the dependence approaches a different type of linear behavior, showing an apparent velocity threshold and a significantly larger slope.

The experimental results provide the most clear and detailed evidence obtained so far of the departure from the velocity proportionality, and indicate a transition between two different regimes in the energy loss process. We propose here a theoretical description of these results and provide a physical explanation of the observed effect.

The simplest theoretical analysis for the energy loss in metals considers the excitation of the conduction electrons (described as a jellium) by a moving ion with velocity  $v$ , producing a stopping force which, in the case of slow ions, may be represented as [2,4]

$$\frac{dE}{dx} = Qv \quad (1)$$

where  $Q$  is the value of the stopping coefficient which for a simple Fermi gas model [2] is given by  $Q = nmv_F\sigma_{tr}$ , where  $n$  is the electron density,  $m$  is the electron mass,  $v_F$  is the Fermi velocity, and  $\sigma_{tr}$  is the momentum transfer cross section. The properties of the electron gas are represented by the Fermi velocity  $v_F$  and/or the usual  $r_s$  parameter, which are related by  $v_F = 1.919/r_s$ . As indicated before, the same type of velocity proportionality is obtained from linear and nonlinear models.

In the present case of the Au target the electronic configuration of the outer shells ( $5d^{10}6s^1$  for free atoms) may be separated into a conduction or free-electron band (of mixed  $s, p$  character) and a *nearly free* band formed by the localized  $d$  electrons [6]. With regard to the conduction band, the description of the electrical properties considers Au as a monovalent metal [17], while a simplified representation considers this band as a Fermi gas with  $r_s = 3.01$  [18]. Thus, we propose first a simplified model (to be referred to as model *a*) to represent the effects of the band structure on the value of the stopping coefficient  $Q$  corresponding to the excitation of both bands (free and  $d$  electrons) as follows:

$$Q^{(a)} = n_1 v_{F_1} \sigma_{tr1} + n_2 v_{F_2} \sigma_{tr2} \quad (2)$$

where  $n_1$  and  $n_2$  are the densities of free and  $d$  electrons,  $v_{F_1}$  and  $v_{F_2}$  are the corresponding Fermi velocities, and  $\sigma_{tr1}$  and  $\sigma_{tr2}$  are the respective momentum-transfer cross sections (MTCS's). The MTCS's are calculated using the expression

$$\sigma_{tr} = \sigma_{tr}(v, U) = 2\pi \int_{\theta_{\min}(U)}^{\pi} |f(\theta)|^2 (1 - \cos \theta) \sin \theta d\theta. \quad (3)$$

Here  $f(\theta)$  is the scattering amplitude given by

$$f(\theta) = \frac{1}{v_r} \sum_l (2l+1) e^{i\delta_l} \sin(\delta_l) P_l(\cos \theta) \quad (4)$$

where  $v_r$  is the electron velocity in the c.m. system and  $\delta_l$  is the phase shift corresponding to the scattering of waves with angular momentum  $l$ . In the present calculations we have used the phase shift values obtained by Puska and Nieminen [19] for each of the corresponding  $r_s$  values that arise from numerical solution of the density functional theory equations. The dependence of  $\sigma_{tr}$  on the ion velocity  $v$  and parameter  $U$  is indicated below.

Note that in Eq. (3) we have introduced a minimum scattering angle  $\theta_{\min}$ . For the usual jellium model this angle is taken as zero, corresponding to the scattering of electrons with negligible energy transfer in the laboratory system which is appropriate for free electrons [first term in Eq. (2)]. In the case of the  $d$  electrons of Au, we take into account the quasifree character, following a previous approach [5], by introducing a minimum energy transfer  $U$ . The connection between  $\theta_{\min}$  and  $U$  may be obtained by considering that a scattering angle  $\theta$  in the c.m. system is associated with an energy transfer  $\Delta E$  (in the laboratory system) given by [20]

$$\Delta E(\theta) = vv_r(1 - \cos \theta) \quad (5)$$

where  $v_r$  is the relative (electron-ion) velocity. Therefore, the minimum scattering angle  $\theta_{\min}$ , corresponding to energy transfers larger than  $U$ , is determined by the condition  $\Delta E(\theta_{\min}) = U$ , which yields  $\cos \theta_{\min} = 1 - U/vv_r$ . Following a previous treatment [3], the mean relative velocity for a slow ion in a Fermi gas was approximated by  $v_r \cong (3/4)v_F$ . Note that by including the energy transfer threshold the friction coefficient  $Q$  becomes a function of velocity.

The physical explanation of the curvature of the stopping curve is based on the analysis of the band structure properties of solid Au, which is represented by the density of states (DOS) corresponding to each band [6]. As may be observed from those calculations, the DOS corresponding to  $d$  electrons shows a significant shift with respect to the Fermi energy  $\varepsilon_F$ , with a spread of energies between 1.5 and 8 eV below  $\varepsilon_F$ . This originates a threshold effect in which the excitation of  $d$  electrons requires a minimum energy transfer, enough to excite the electron to unoccupied states over the Fermi level.

To incorporate in a more realistic way the properties of the band structures of gold we performed a more detailed calculation (denoted as model  $b$ ), integrating the energy transfer to  $s$ ,  $p$ , and  $d$  electrons, using the corresponding DOS distributions [6,21]  $n_{sp}(\varepsilon)$  and  $n_d(\varepsilon)$  which leads to a stopping coefficient of the form

$$Q^{(b)} = v_F^{(s,p)} \int_0^{\varepsilon_F} \sigma_{tr}(v, U_\varepsilon) n_{sp}(\varepsilon) d\varepsilon + v_F^{(d)} \int_0^{\varepsilon_F} \sigma_{tr}(v, U_\varepsilon) n_d(\varepsilon) d\varepsilon \quad (6)$$

where  $U_\varepsilon = \varepsilon_F - \varepsilon$  is the threshold imposed on the momentum transfer cross section  $\sigma_{tr}$  in order to restrict the excitation of electrons with initial energies  $\varepsilon$  to allowed final states with energies over the Fermi level  $\varepsilon_F$ .

The results of the various model calculations together with the experimental stopping power results are shown in Fig. 2. To provide a complete analysis and comparison, the first theoretical estimation considers all the electrons ( $s, p, d$ ) as fully free and calculates the stopping coefficient using the DFT results of Ref. [19] with an effective value of  $r_s = 1.8$  a.u., which represents an average value of the local density in the  $\langle 100 \rangle$  channel of Au according to numerical simulations reported before [16]. This first estimation is indicated by a dotted line in Fig. 2. The result serves to illustrate the proportionality with ion velocity predicted by the standard DFT.

The second estimation is that of model  $a$ , Eq. (2), where the excitation of free ( $s, p$ ) electrons is calculated without energy threshold ( $U=0$ ), while the excitation of  $d$  electrons is modified by the threshold effect in a rather simple way using a constant value  $U=6$  eV for all the  $d$  electrons. In order to emphasize the shape of the stopping curve rather than the absolute values, the calculations have been normalized to the experiments at the velocity  $v=0.6$  a.u. For this estimation we have used fixed values  $r_s=3.01$  and  $r_s=2$  for the free ( $s, p$ ) and  $d$  electron components, respectively. As explained before, the first value is the one corresponding to

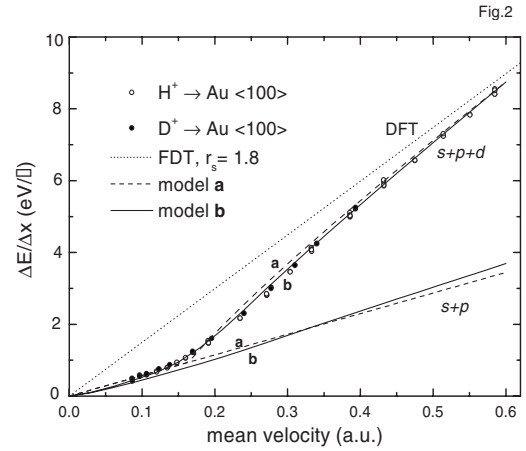


FIG. 2. Comparison between experimental and theoretical results for the energy loss of channelled protons and deuterons in Au, as described in the text. Dotted line: calculations according to the DFT approach for a simple model with  $r_s=1.8$ . Dashed line: result of model  $a$  considering two components, free electrons with  $r_s=3$  and  $U=0$ , and nearly free electrons with  $r_s=2$  and  $U=6$  eV. Solid line: result of model  $b$  where the contributions of  $s$ ,  $p$ , and  $d$  electrons are evaluated by numerical integrations using the calculated densities of states (see text for further details). The data points are the experimental results from Fig. 1.

the normal density of conduction electrons in Au [18] while the second  $r_s$  value is the one required to reproduce the effective density in the channel corresponding to  $r_s=1.8$  (by the addition of the two electron density components, and in consistency with the previous DFT estimation).

Finally, the third calculation is that of model  $b$ , where a full integration over the densities of states corresponding to  $s$ ,  $p$ , and  $d$  electrons has been performed, including the minimum excitation energy  $U_\varepsilon$  in the calculation of  $\sigma_{tr}$ . The normalization of the theoretical values was made with the same criterion as before. The lower dashed and solid lines in the figure show the contributions of the free-electron component according to the two models [first term in Eqs. (2) and (6)]. The contribution of these electrons yields a strict proportionality with ion velocity in model  $a$  and a small deviation from this dependence in model  $b$ .

The upper  $a$  and  $b$  lines show the total energy loss according to both models. We observe that the calculations based on model  $b$  yield an excellent representation of the shape of the energy loss curve, while those of model  $a$  give a more schematic but also consistent description of the experimental features. We stress that the good description of the shape of the stopping curve relies, in the case of model  $a$ , on the assumed values of  $r_s$ , whose justification was already indicated, and, in the case of model  $b$ , on the realistic band structure properties represented by the DOS, obtained from independent calculations, not including any fitting parameter. The model explains the threshold behavior and the transition between the two nearly linear velocity dependences.

In summary, from high-precision measurements of the energy loss of slow protons and deuterons in channeling conditions on very thin crystals of gold, we have explored, using the ion transmission technique, the lowest energy range so

far accessed to our knowledge. In this way, we have obtained clear evidence of the transition between two well-defined regimes in the low-energy extreme of the stopping curve, which generates a significant deviation from the velocity proportionality. We provide a theoretical explanation of this effect by separating the contributions of free ( $s, p$ ) and nearly free ( $d$ ) electrons according to calculations of the density of states for solid Au [21].

The theoretical calculations explain the change in the behavior of the stopping curve as due to a transition from an upper velocity range (but still lower than  $v_0$ ) where  $s, p$ , and  $d$  electrons can be excited, to a lower energy range where only the free ( $s, p$ ) electron component may be excited. This produces a change in the slope of the stopping curve and gives rise to an apparent threshold in the energy loss which cannot be explained by the usual free-electron theories. The magnitude of the effect and the position of the transition

between both stopping regimes is very well explained by the present theoretical model. Only the lowest velocity region ( $v < 0.15$  a.u.) shows the type of velocity proportionality predicted by DFT and other free-electron gas models.

In a more general context, we have shown that the behavior of the low-energy stopping coefficient is strongly influenced by the properties of the electronic band structure of the target material. The present study for a metallic sample may also give some hints of interest for the theoretical treatment of apparently related threshold effects in insulators.

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