Comparative study of the stopping power of graphite and diamond

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The stopping cross section of graphite and diamond for hydrogen and helium projectiles in the energy range $20 < E < 80$ keV/amu has been measured. It is found that in the case of graphite the stopping cross section for protons is up to 40% larger than that of diamond, while for He projectiles the difference is about one-half of that. The results are explained using the charge-state approach to stopping, that includes in an approximate manner the energy loss in charge-exchange processes and a simple model for the valence-electron excitations of the two allotropic forms of carbon. [S0163-1829(97)07119-1]

I. INTRODUCTION

The stopping power for low atomic number materials and light incident ions depends on the physical and chemical state of the sample, especially when the velocity of the incident ion is about the Fermi velocity of the material. The interaction of the incident ion with the solid can be divided into two parts: one is due to the interaction with the valence electrons, and the other is due to the interaction with the ion cores. The first one plays an important role in the range of velocities under consideration, and therefore the stopping power depends strongly on the state of the sample. One of the best-suited materials to study these effects is carbon, which can be found in several allotropic forms: graphite, amorphous carbon, diamond, and fullerenes. In this work we present the experimentally measured and theoretically calculated stopping cross sections of diamond and graphite for protons, as well as the ratio of the stopping cross sections for alpha particles in a narrow energy range, in order to investigate the allotropic effect.

The plasmon losses of diamond and graphite, well known in literature, are found to be 35 and 27 eV, respectively. It should be noted that these plasmon energies are not too far from the values obtained in the free-electron-gas model from the atomic densities $n_A$ of these materials, assuming a number of four electrons per atom contributing to the plasmon. For a summary of the properties of different carbon phases, see Table I. The values of the plasmon energies are rather large, corresponding to rather high densities (and low $r_S$ values, where $r_S$ is defined from the valence electron density $n_{el}$ by $r_S = [3/4\pi n_{el}]^{1/3}$). An allotropic effect is clearly to be expected, in terms of stopping power as well as in terms of the stopping cross section. The allotropic effect in the stopping power is of the opposite direction compared to the stopping cross section. In the stopping power the density enters twofold, via the number of collision partners and via the strength of the interactions. The trivial density dependence (i.e., the number of collision partners per unit length) is removed when looking at the cross section. Thus, in terms of physics, the stopping cross section is more illuminative than the stopping power.

II. EXPERIMENT

Similarly to our earlier measurements on oxides and on amorphous carbon the stopping cross section was measured by Rutherford backscattering (RBS) comparing the spectrum heights obtained from two targets for the same incident charge. He$^+$ and H$^+$ ions of velocities around $v_0 (= c/137)$ are used as projectiles, highly oriented pyrolytic graphite (HOPG) and polished natural diamond have been used as target materials. The choice of targets of the same atomic number simplifies the data evaluation, because the scattering cross section and the kinematic factor are identical in both

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<th>Table I. Electronic and structural properties for the two carbon phases.</th>
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<td>Mass density $\rho$ (g/cm$^3$)</td>
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targets, and the spectrum heights are expected to differ only because of different stopping cross sections. Both targets were exposed to the same amount of primary ions, and the stopping information was extracted from the spectrum heights. Special care was taken to ensure reliability of the ion current integration using the setup described earlier. Repeated test runs showed reproducibility and consistency of the resulting ion charge values within 1%.

To extract the stopping information from the spectrum heights is only possible in case that channeling in these materials is avoided. This is not trivial, because both diamond and graphite have crystal directions in which channeling can occur. In the HOPG used, to avoid channeling is simpler, because here only perpendicular incidence and exit of the projectiles will lead to channeling and blocking, respectively. In diamond, proper crystal directions for which randomlike spectra are observed have to be searched carefully. In detailed angular scans those directions have been selected for which the height of the high-energy edge of the measured spectrum coincides within 3% with that expected for an amorphous target as obtained from computer simulations, analogously to our measurements on LiNbO$_3$. The reason to choose natural diamond was that this material is quite pure without any hydrogen contamination as in other types of artificial diamonds.

From the heights of the RBS spectra of graphite, $H_{\text{gra}}$, and of diamond, $H_{\text{dia}}$, the ratio of the stopping cross sections in graphite $S_{\text{gra}}$ and diamond $S_{\text{dia}}$ follows from

$$\frac{H_{\text{gra}}}{H_{\text{dia}} = \frac{S_{\text{dia}}(E_1)}{S_{\text{gra}}(E_1)},}$$

where $E_1$ is a mean energy which may be determined following Ref. 6. We stress the point that, in this special case, where the kinematic factor is identical for both targets, the systematic errors of evaluating $S_{\text{dia}}/S_{\text{gra}}$ from the previous equation are negligible because they cancel each other to high precision. The evaluation of the spectrum heights was done as described in Ref. 2.

The uncertainty of the resulting ratios $S_{\text{dia}}/S_{\text{gra}}$ is estimated to be 5%, containing contributions from current integration$^4$ (±1%), the determination of the spectrum height (±3%), and a possible residual influence of channeling in diamond (±3%). This estimate is in concordance with the observed scatter of the experimental data. For hydrogen projectiles, we can use our earlier measurements of the stopping ratio$^3$ of graphite and amorphous carbon, $S_{\text{gra}}/S_{\text{am}}$, to obtain absolute values $S_{\text{dia}}$ and $S_{\text{gra}}$, but with a somewhat larger uncertainty (7%). The measurements for H$^+$ ions were done using protons and deuterons which are known to have identical stopping properties at the same speed. In order to present the results of both projectiles in the same figure, we plot the stopping cross section for H$^+$ ions as a function of $E/A$, where $E$ denotes the mean energy and $A$ the number of nucleons. For He ions, only $^4\text{He}^+$ projectiles have been used, therefore in this case the mean energy of $^4\text{He}^+$ projectiles is used as abscissa.

### III. THEORETICAL CALCULATIONS

The energy-loss calculation in solids is a complicated problem due to its many-body character, and especially in the energy region where the maximum of the stopping is located ($v \equiv Z_1^{2/3} v_0$). In this region there is a succession of electron capture and loss events by the incident ion which complicates the treatment. As a consequence the charge state of the incident ion beam is modified. If the thickness of the sample is larger than a minimum value an equilibrium charge state distribution independent of the initial state of the beam is reached. The population of the different charge states can be calculated from the capture and loss rates (probability per unit time of having a capture or a loss event respectively, $\Gamma_{c,l}$). Associated with the charge changing processes there is an additional energy loss that can be calculated in a similar way as the capture and loss probabilities.$^7$ It typically amounts for 10–20% of the total losses as long as $Z_1 \ll Z_2$:

$$\frac{dE}{dR}_{c,l} = \frac{1}{v} \int d\omega \omega \frac{d\Gamma_{c,l}}{d\omega},$$

where $\omega$ is the electron transition energy (atomic units are used for the theoretical expressions). In the energy range that we consider, hydrogen projectiles can be found in two different charge states: H$^0$ and H$^+$. So the energy loss can be written as a weighted sum

$$\frac{dE}{dR} = \Phi^0 \frac{dE}{dR}_{c}(\text{H}^0) + \Phi^+ \frac{dE}{dR}_{c}(\text{H}^+) + \Phi^0 \frac{dE}{dR}_{l}(\text{H}^0) + \Phi^+ \frac{dE}{dR}_{l}(\text{H}^+).$$

The total energy loss is the addition of the energy losses associated with each charge state (weighted by its corresponding fraction $\Phi^{0,\pm}$), plus the one due to the capture and loss processes. For He projectiles, He$^0$ and He$^+$ are to be used instead of H$^0$ and H$^+$. The He energy loss, above 100 keV, is mostly due to target electron excitations by He$^+$ ions.

We use an electron-gas model for the target to represent the valence-electron excitations of carbon with two different densities for diamond and graphite, respectively (see Table I). Strictly speaking, the electrons are not free, but as long as the gap energy is small compared to the plasmon energy and to the mean transition energies ($\approx \mu v u v$), we regard the valence electrons as nearly free.

The energy loss of the He$^+$ and H$^+$ ions is calculated in the dielectric formalism using a random-phase-approximation (RPA) dielectric function with the corresponding density parameter for each material. This treatment includes both electron-hole pair and plasmon excitations in a self-consistent way.$^8$ The dielectric approach can be used as long as only the H$^+$ fraction is relevant, i.e., at high velocities. In the case of He$^+$ ions we also account for the screening by the electron bound to the projectile.$^9$

We have calculated $dE/dR$ (H$^0$) by independently obtaining contributions from the electron-hole pairs and those from the plasmon excitations. The former is obtained using a binary encounter approximation.$^1$ The plasmon contribution, although small, is obtained in linear theory using the RPA dielectric function, taking into account that nonlinear effects are only important at low ion velocities. In order to calculate
the equilibrium charge-state distribution for protons we have considered two kinds of processes that can lead to a charge-exchange event.

(a) Auger processes. An electron can be captured or lost by the incident ion due to the interaction with the valence-band electrons, inducing at the same time an excitation in the band electron-hole pairs or plasmons.

(b) Resonant processes which are due to the interaction of the ions with the lattice. The interaction potential is seen by the incident ion as a time-dependent periodic potential that can induce transitions between the bound states of the ion and the continuum states.

Those processes where inner shell electrons of the lattice ions can be captured by the incident ion are not important at these energies, as the carbon K-shell electrons are bound by 284 eV.

In the case of diamond we calculated the probabilities for the capture and loss events by the previously described mechanisms. The response of the valence band is represented by a RPA dielectric function with the appropriate parameter (Table I). The ions are organized in a face-centered-cubic lattice with a basis, and we represent the interaction potential by a statically screened Thomas-Fermi one,

$$V(q) = \frac{4\pi}{q^2 + k_{TF}^2} \left[ Z_2 - \frac{2}{1 + (q/2a_k)^2} \right],$$

where $Z_2 = 6$, $a_k = 5.7$, and $k_{TF}$ is the Thomas-Fermi screening wave vector.

For the graphite we used charge-state fraction data available in the literature. We know from calculations in some other materials and in diamond that in the case of protons at these energies the resonant capture probabilities are much smaller than the Auger ones; thus we approximate $\sigma_c = \sigma_c^A + \sigma_c^R = \sigma_c^A$. We calculated the Auger process cross sections using the corresponding electron-gas density (Table I). From the experimental charge-state fractions one can deduce the cross section for the loss events:

$$\sigma_L = \Phi^+ \sigma_c^A$$

where $\sigma_c = \sigma_c^A$.

The stopping cross section associated with the capture and loss processes, $S_{C,L}$, can be obtained by multiplying the cross section, $\sigma_{C,L}$, by a mean transition energy for the capture and loss events, respectively,

$$S_C = \sigma_c \Delta E_c = \sigma_c \left( \frac{v^2}{2} \right),$$

$$S_L = \sigma_L \Delta E_L = \sigma_L E_b,$$

where $E_b$ is the binding energy of the electron lost by the incident ion.

IV. RESULTS

In Fig. 1 we show the stopping cross section for protons in diamond as a function of the incident ion energy. The dots represent experimental results, and the curve labeled TOTAL is the theoretical calculation. The curves $H^0$, $H^+$, and C&L represent each partial contribution to the stopping cross section. The agreement is rather good except in the lowest energy region. In the low-velocity region the $H^0$ contribution

FIG. 1. Stopping cross section (in $10^{-15}$ eV cm$^2$) of diamond for protons. The curve labeled total is the result of the theoretical calculation, while the squares are experimental data. $H^+$ and $H^0$ refer to the contributions from $H^+$ and $H^0$ to the total stopping. C&L is the contribution from capture and loss processes.

FIG. 2. Same as Fig. 1 for graphite instead of diamond.

FIG. 3. Ratio of the stopping cross sections of graphite and diamond for protons.
dominates the stopping cross section while it becomes negligible in the high velocity range which is dominated by the H\(^+\) contribution. The C\&L cross section has its maximum value at velocities close to the Fermi velocity \(\langle m_{e}\nu F^2/2 \equiv 60 \text{ keV} \rangle\), where it is about a 10\% of the total stopping cross section.

Figure 2 is equivalent to the previous one, but it shows the values for graphite. We again find a worse agreement in the low-energy range. The behavior of the C\&L curve is not so reliable at low energies, which is partially due to the fact that we have used approximate mean transition energies to calculate the capture and loss contribution.

In Fig. 3 the theoretical and experimental results for the ratio of the graphite and for diamond stopping cross sections are represented together. The picture shows clearly the existence of a noticeable allotropic effect in the stopping cross section. The stopping ratio observed comparing the results for the two materials is about 25–30\%, and is very well reproduced by the theoretical results, even though there is a discrepancy between experimental and theoretical values for each material.

In Fig. 4 we show the ratio of the stopping cross sections of diamond and graphite for He ions. The continuous curve is the calculated one for He\(^+\) ions, while the different symbols correspond to the experimental data in the energy range 80 keV < \(E < 280 \text{ keV}\). There is a fair agreement between the theory and the experimental data.

**V. CONCLUSIONS**

The different stopping cross sections of graphite and diamond for protons have been successfully explained using the charge-state approach.\(^6\) Although we typically overestimate the values of both the two cross sections and find a larger discrepancy at the lower velocities, we consider that the agreement between theory and experiment is quite satisfactory considering the simplicity of the model, particularly the way of treating the energy loss in charge-changing processes. It is worth mentioning that the ratio of the atomic densities of diamond and graphite is 1.56, which shows that the protons are more efficiently slowed down in the case of diamond, as the measured difference in stopping cross section is below 50\%. In conclusion, although diamond has a band gap in its electronic excitation spectrum (\(\approx 4 \text{ eV}\)) and graphite has a much smaller one (\(\approx 1 \text{ eV}\)), these gaps are not relevant as far as electronic stopping is concerned in this energy range (\(E > 20 \text{ keV}\)), and the energy loss of hydrogen ions may be interpreted in terms of a free-electron-gas description.\(^{13}\)

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