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Proton energy loss in allotropic forms of carbon

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We have investigated theoretically the electronic stopping of protons in different solid forms of carbon: glassy, amorphous, graphite, diamond and C_{60}-fullerite. The energy loss is described within the dielectric formalism and the target properties are modelled by a sum of Mermin-type energy loss functions. For each allotropic carbon form, we observe remarkable differences in the stopping cross section and in the energy loss straggling at proton velocities around and lower than that corresponding to the maximum in the energy loss. A comparison of our results with available experimental data shows a reasonably good agreement.

Carbon is a substance that appears in nature, or may be produced in the laboratory, in many diverse forms and with many different properties. This is a consequence of the ability of carbon-based materials to form bonds with various types of sp-hybridization. Carbon, in its diverse allotropic forms, is widely used as a target in experiments of ion bombardment of solids, where effects related with density, structure or optical properties, among others, play a significative role. Therefore, an accurate description of the response of the different carbon targets to external perturbations is needed in order to provide a more realistic representation of the energy loss processes in each material.

The electronic energy loss processes experienced by a charged particle penetrating in a medium can be described within the dielectric formalism [1]. In this framework the main parameter is the dielectric function, that describes the response of the material to external perturbations. Lindhard [2], making use of the random phase approximation, derived an expression for the dielectric function in which the electron gas can sustain plasmons (collective excitations) and electron–hole pair (i.e., individual) excitations. However such a dielectric function does not take into account the finite lifetime of the plasmons, therefore individual and collective excitations are decoupled in the dispersion relation. Mermin [3] provided a modification to the Lindhard dielectric function which avoided the aforementioned restrictions, so allowing for the decay of plasmons into electron–hole excitations. Mermin's dielectric function [3], ϵ_M, is characterized by two parameters: the plasmon frequency ω_p (related with the material density ρ) and the damping γ of the plasma oscillations.

The energy loss function $\mathrm{Im}(-1/\epsilon)$, ELF hereafter, derived from the Mermin dielectric function has only one well defined peak, which is in contrast with most of the experimentally recorded energy loss spectra [4,5] and, in particular, for carbon targets. To overcome this problem we fit the experimental energy loss spectrum at zero wave number, $k = 0$, by a sum of Mermin-type ELF, which allows the inclusion of different peaks in the ELF,

$$\mathrm{Im}\left[\frac{-1}{\epsilon(k=0,\omega)}\right]_{\mathrm{exp}} \cong \sum_{i=1}^{n} A_i \,\mathrm{Im}\left[\frac{-1}{\epsilon_M(\omega_{pi},\gamma_i;k=0,\omega)}\right], \qquad (1)$$

where ω_{pi} and γ_i are related to the location and width, respectively, of each peak in the energy loss spectrum. The weights A_i are chosen in such a manner that the sum rule for the effective number of electrons in the medium is satisfied. A similar procedure was adopted by Ashley et al. [6] using a sum of Drude-type ELF, and an analytical extension of $\omega_{pi}(k)$ and $\gamma_i(k)$ to $k \neq 0$ values.

Assuming that the main contribution to the pro-

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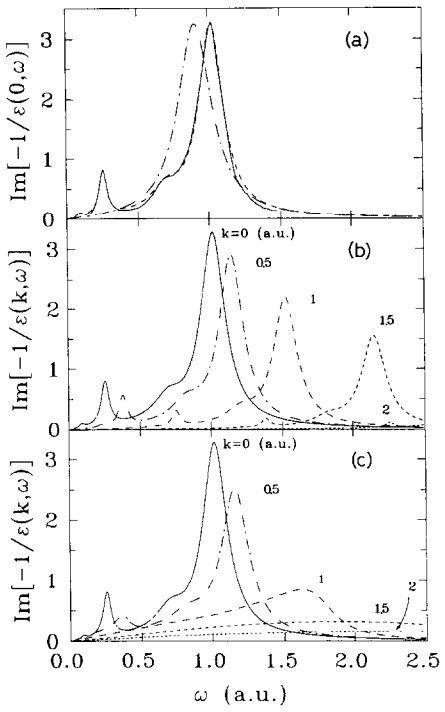

Fig. 1. Energy loss function $\mathrm{Im}[-1/\epsilon(k,\omega)]$ of graphite as a function of excitation frequency. (a) Experimental data at $k = 0$ [7] (solid line), sum of Mermin-type ELF (dashed line) and a single Mermin-type ELF (dash-dotted line). (b) Sum of Drude-type ELF for different values of the wave number k. (c) Sum of Mermin-type ELF for different values of the wave number k.

ton energy loss comes from electronic excitations, the stopping power S_p and the energy-loss straggling Ω^2 for a proton moving with velocity v through a medium characterized by an energy loss function $\mathrm{Im}[-1/\epsilon(k,\omega)]$, are written [2], respectively, as

$$S_p = \frac{2}{\pi^2 v}\int_0^\infty \frac{dk}{k}\int_0^{kv} d\omega\,\omega\,\mathrm{Im}\left[\frac{-1}{\epsilon(k,\omega)}\right] \qquad (2)$$

and

$$\Omega^2 = \frac{2}{\pi^2 v}\int_0^\infty \frac{dk}{k}\int_0^{kv} d\omega\,\omega^2\,\mathrm{Im}\left[\frac{-1}{\epsilon(k,\omega)}\right]. \qquad (3)$$

Note that atomic units ($e = \hbar = m_e = 1$) are used throughout this paper.

For each allotropic form of carbon, we fitted the experimental ELF by a sum of Mermin-type ELF, according to eq. (1). We have considered glassy carbon ($\rho = 1.459$ g/cm^3) [7], amorphous carbon ($\rho = 1.68$ g/cm^3) [8], graphite ($\rho = 2.25$ g/cm^3) [7], diamond ($\rho = 3.515$ g/cm^3) [7], and C_{60}-fullerite ($\rho = 1.678$ g/cm^3) [9].

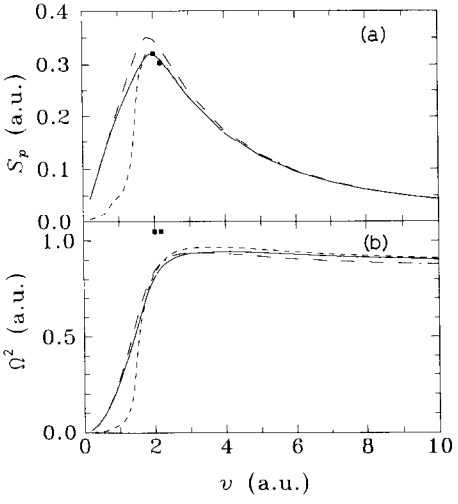

Fig. 2. (a) Stopping power S_p and (b) energy loss straggling Ω^2 as a function of proton velocity for a graphite target. The calculations have been done with a sum of Mermin-type ELF (solid line), a single Mermin-type ELF (dash-dotted line), and a sum of Drude-type ELF (dashed line). The squares are experimental data from ref. [15].

The case of graphite is illustrated in Fig. 1. The experimental ELF [7] at $k = 0$ appears as a continuum line in Fig. 1a, together with the fitted curve corresponding to a sum of Mermin-type ELF (dashed line), and with a single Mermin-type ELF for $\omega_p = 0.92$ a.u. and $\gamma = 0.285$ a.u. (dash-dotted line). It can be appreciated how the main peak in the ELF is shifted in the single Mermin approach with respect to the experimental one and, moreover, the low energy peak is absent. Figs. 1b and 1c show the behaviour of the fitted ELF, for various values of the wave number k, when a sum of Drude-type ELF [6], ϵ_D-ELF, or a sum of Mermin-type ELF, ϵ_M-ELF, are used, respectively. Although both the ELF fitted by a sum of ϵ_M-ELF or by a sum of ϵ_D-ELF coincide at $k = 0$, their evolution with the wave number k is dramatically different. The structure of the sum of ϵ_D-ELF at $k = 0$ is retained when the wave number increases (Fig. 1b); however, this structure gradually disappears in the case of the sum of ϵ_M-ELF (Fig. 1c). It is worth noting that the ELF obtained from a sum of ϵ_M-ELF or from a single ϵ_M-ELF are very similar for $k \geq 1$ a.u.

The calculated stopping power, S_p and the energy loss straggling, Ω^2, corresponding to a proton moving with velocity v through graphite have been plotted in Fig. 2. The calculations where done using in Eqs. (2) and (3) the three different models for $\mathrm{Im}[-1/\epsilon(k,\omega)]$ previously mentioned, i.e, a sum of ϵ_M-ELF (solid line), a sum of ϵ_D-ELF (dashed line)

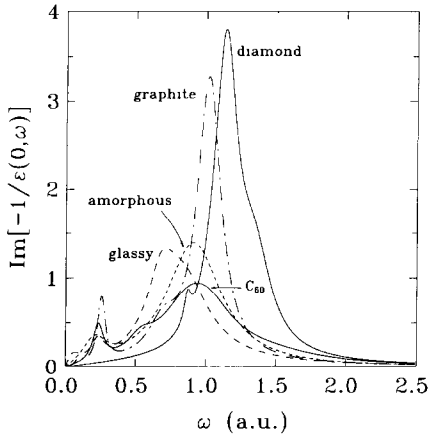

Fig. 3. Energy loss function $\mathrm{Im}[-1/\epsilon(k=0,\omega)]$ modelled as a sum of ϵ_M-ELF for several carbon species: glassy, amorphous, graphite, diamond and C_{60}-fullerite.

and a single ϵ_M-ELF (dash-dotted line). In Fig. 2a we observe how all these models provide almost the same stopping power at high proton velocities; this is so because the sum rules for the effective number of valence electrons (4 for carbon) are satisfied in the three models. At low velocities ($v \leq 1$ a.u.) the stopping power S_p is proportional to the proton velocity, as is known experimentally [10–14], for both a sum of and a single ϵ_M-ELF. This is due to the fact that the principal contributions to the energy loss are due to electron–hole pair excitations, described correctly by Mermin's dielectric formalism. This argument also explains the incorrect behaviour of S_p obtained from the sum of ϵ_D-ELF model [6], since the Drude dielectric function describes well the collective excitations (plasmons) but not the low-energy single-particle excitations. The stopping power predicted by a sum of ϵ_M-ELF around the maximum of the stopping ($v \sim 2$ a.u.) agrees very well with the experimental data [15], however, the results obtained by a single ϵ_M-ELF overestimates these data. Practically the same comments are valid for the energy loss straggling, Ω^2, depicted in Fig. 2b, where it can be seen that the ϵ_M-ELF model gives the correct behavior $\Omega^2 \sim v^2$ at low velocities.

We conclude that the present model based on a sum of ϵ_M-ELF gives a correct description of the stopping power and the energy loss straggling at low, medium and high proton velocities. Using this model we have plotted in Fig. 3 the sum of ϵ_M-ELF for five allotropes of carbon: glassy carbon [7], amorphous carbon [8], graphite [7], diamond [7], and C_{60}-fullerite [9]. Two well defined peaks can easily be seen, one at low energy ($\sim$ 7 eV) associated with the π electrons and the other at high energy ($\sim$ 25 eV) associated with the $\pi + \sigma$ electrons. These peaks are common, with variable

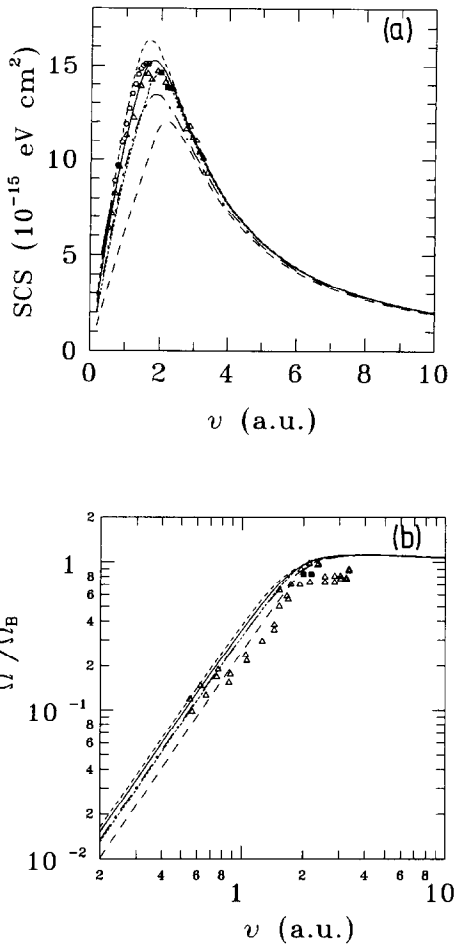

Fig. 4. (a) Stopping cross section (SCS) and (b) normalized energy loss straggling (Ω^2/Ω_B^2) as a function of proton velocity for different carbon targets: glassy (- - -), amorphous (—), graphite (···), C_{60}-fullerite (- · - · -) and diamond (– – –). A sum of Mermin-type ELF was used in the calculations. Experimental data: ■ ref. [15], △ ref. [16], —— ref. [17], ○ ref. [18].

intensity, to all carbon allotropes with sp^2-bonds. The case of diamond, with only sp^3-bonds and no free π electrons shows only the high energy peak.

According to the ELF shown in Fig. 3 we have plotted in Fig. 4a the stopping cross section, SCS, and in Fig. 4b the normalized energy loss straggling, Ω^2/Ω_B^2 (where Ω_B^2 is the Bohr straggling), corresponding to several carbon targets. At proton velocities $v \leq 2$ a.u. our calculations for the five allotropes of carbon show differences in the SCS ranging from $\sim$ 50% to $\sim$ 100%, being larger in the low velocity region. However, these differences are not so noticeable in the case of the Ω^2/Ω_B^2. We also compare with experimental data, although some references did not always provide information on the type of carbon targets

used in the measurements. The agreement between our calculations and the experiments for graphite and amorphous carbon [15–18] is reasonably good in the SCS. Especially remarkable is the case of amorphous carbon, where the calculated and the experimental [16–18] SCS values lie practically on the same curve, except around the maximum, where the experimental data are slightly scattered. Some discrepancies are observed in Fig. 4b for Ω^2/Ω_B^2, but the difficulty in determining experimentally the energy loss straggling it is well known. The experimental ratio $SCS_{graphite}/SCS_{diamond} = 1.06$ obtained for 1.1 MeV protons [19] compares well with the value 1.04 derived from our calculations. For carbon projectiles with velocities between 3 a.u. and 4 a.u. the ratios $SCS_{graphite}/SCS_{diamond}$ and $SCS_{glassy\ carbon}/SCS_{diamond}$, were found [20] to be 1.036 and 1.072, respectively; these results show the same trends than our calculations (1.08 and 1.1, respectively, for $v = 3$ a.u.). The stopping cross section and the normalized energy loss straggling of the five carbon modifications studied in this work become larger in the order diamond, C_{60}-fullerite, graphite, amorphous carbon and glassy carbon, but the results for graphite and C_{60}-fullerite are very similar at low velocities; the same ordering of the SCS was determined by Baek et al. [20] when bombarding diamond, graphite and glassy carbon with carbon projectiles at intermediate velocities. These results reveal the influence of the bonding-type of the different allotropes on the energy loss.

In conclusion, we have presented a model, based in a sum of ϵ_M-type ELF, to describe in a more realistic way the energy loss of protons in a wide range of velocities for different allotropes of carbon. The results provided by the model agree fairly well with the available experimental data, and although non-linear effects may become important at low velocities, its evaluation would require a more sophisticated treatment which is beyond the scope of the present work.

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References

[1] D. Pines, Elementary Excitations in Solids (Benjamin, New York, 1964).
[2] J. Lindhard, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 28 (1954) no. 8.
[3] N.D. Mermin, Phys. Rev. B 1 (1970) 2362.
[4] K.D. Sevier, Low Energy Electron Spectrometry (Wiley-Interscience, New York, 1972).
[5] R. Raether, Excitations of Plasmons and Interband Transitions by Electrons, Springer Tracts in Modern Physics, Vol. 88 (Springer, Berlin, 1980).
[6] J.C. Ashley, J.J. Cowan, R.H. Ritchie, V.E. Anderson and J. Hoelzl, Thin Solid Films 60 (1979) 361.
[7] J. Tung and C. Lin, Radiat. Eff. 80 (1980) 261.
[8] J. Cazaux and D. Gramari, J. de Phys. 38 (1977) L133.
[9] R. Kuzuo, M. Terauchi, M. Tanaka, Y. Saito and H. Shinohara, Jpn. J. Appl. Phys. 30 (1991) L1817.
[10] W. Bernstein, A.J. Cole and R.L. Ward, Nucl. Instr. and Meth. 90 (1970) 325.
[11] E.P. Arkhipov and Y.V. Gott, Sov. Phys. JETP 29 (1969) 615.
[12] G. Hogberg, Phys. Status Solidi B 48 (1971) 829.
[13] S. Mikheev, Y. Ryzhov, I. Shkarban and V. Yurasova, Nucl. Instr. and Meth. B 78 (1993) 86.
[14] H. Grahmann and S. Kalbitzer, Nucl. Instr. and Meth. 132 (1976) 119.
[15] N. Matsunami and K. Kitoh, Nucl. Instr. and Meth. B 67 (1992) 50.
[16] J. Shchuchinsky and C. Peterson, Radiat. Eff. 81 (1984) 221.
[17] R. Golser, Ch. Eppacher and D. Semrad, Nucl. Instr. and Meth. B 67 (1992) 69.
[18] J.H. Ormrod and H.E. Duckworth, Can. J. Phys. 41 (1963) 1424.
[19] S.D. Softky, Phys. Rev. 123 (1961) 1685.
[20] W.Y. Baek, G.H. Both, D. Gassen, W. Neuwirth and M. Zielinski, Phys. Rev. A 35 (1987) 51.