Isotopic Mass Effects for Low-Energy Ion Channeling in Single-Wall Carbon Nanotubes

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Monte Carlo (MC) simulation studies of isotopic mass effects have been conducted, for low-energy channeling of ^{12}C and ^{13}C ions in single-wall carbon nanotubes. It is found in MC simulations that ($\Psi_{C\ for\ ^{12}C}/\Psi_{C\ for\ ^{13}C}$) = $(13/12)^{1/2}$, for the same incident energies. Here, $\Psi_{C\ for\ ^{12}C}$ is the critical angle for ^{12}C channeling, and $\Psi_{C\ for\ ^{13}C}$ is the critical angle for ^{13}C channeling. This work shows the mass effect to be the incident momentum one, but a recent work (Moura, C. S.; Amaral, L. *J. Phys. Chem. B* **2005**, *109*, 13515) considered it to be the energy transfer effect. Our work disagrees with that of Moura and Amaral.

1. Introduction

Carbon nanotubes were discovered in 1991;[1] two years later, a process for the production of so-called single-wall carbon nanotubes (SWCNTs) was discovered,[2] as compared with an earlier sample containing multiwall carbon nanotubes (MWCNTs). Because of their superlattice structures, channeling of particles in nanotubes exhibits a number of special features associated with the relatively large diameter of the channels and a weaker influence of dechanneling factors than in ordinary crystals. These features have already been exploited, for instance, in semiconductor technologies, particle accelerators, and radiation sources of hard X-rays.[3−15]

It is well-known that low-energy collision fields include sputtering and channeling fields, etc. It is now recognized that mass effects, i.e., momentum effects, may play an important role in these fields. For example, approximately 20 years ago, for the zero-fluence, i.e., low-fluence limit, isotope sputtering, simulations[16−18] showed the preferential emission of lighter isotopes in the near-normal direction as a primary effect and, interestingly, showed a substantial momentum asymmetry between the light atoms in the cascade and the heavy one.[16] In 1993, collector-type experiments[19] were conducted using isotopically enriched $^{92}Mo-^{100}Mo$ targets to investigate the primary effect in sputtering induced by 5 and 10 keV Ar^+ and Xe^+ ions and showed, for example, that the difference between the near-normal isotopic ratio and the oblique isotopic ratio was positive and as great as 3.05% at a fluence range of $0-0.30 \times 10^{15}$ ions/cm^2 for 5 keV Xe^+ ion bombardment. Later, the simulations[20−24] agreed quantitatively with this experimental evidence[19] for the primary effect on the isotopic fractionation. In short, the momentum effects, i.e., the momentum asymmetry effects, may produce the isotopic angular pattern.

Recently, for low-energy ion channeling, the first experiment[9] showed the channeling critical angle to be 1.5° for a 2 MeV He^+ micrometer-sized beam propagating into the MWCNT rope. According to eq 1 of ref 11 if the channeling critical angle equals $67E^{-1/2}$, it satisfies the experimental result of ref 9. The molecular dynamics (MD) simulation[11] has shown this angle to equal $20E^{-1/2}$ for a 1−20 keV Ar nanometer-sized beam propagating into the SWCNT, and the MC simulation[25] has shown this angle to equal $48E^{-1/2}$ for a 10−550 keV He nanometer-sized beam propagating into the SWCNT. In other words, MD and MC simulation works have shown that the critical angles for channeling Ψ_C turn out to be much smaller for the heavier (Ar) ion than for the lighter (He) one, because, in our opinion, the larger the ion mass, the larger the transverse incident momentum. However, the experiment and simulation works disagree with the theories,[26−29] because the theories have shown that the critical angles for channeling Ψ_C turn out to be much smaller for the smaller nucleus charge of the ion (He) than for the larger one (Ar). In this work, we have simulated the channeling of isotopic ^{12}C and ^{13}C ions in the SWCNT, to focus the mass effects, i.e., the incident momentum effects, on the critical angles for channeling Ψ_C.

Our recent works[25,30] showed the mass effect to be the incident momentum one, but ref 13 considered it to be the energy transfer effect. Our works disagreed with ref 13.

2. Simulation Program Series

Our MC simulation program series has been employed in investigating particle motions exclusively along a straight-line segment in amorphous and crystalline[25,30−34] materials. This MC simulation program[25,30] utilizes a binary collision model based on the Moliere potential for the ion−atom (or atom−atom) interactions and on the continuously slowing approximation for electronic stopping, at low temperatures. Nanotubes in a superlattice are kept in a position of equilibrium by van der Waals forces, and the gap between the walls of neighboring nanotubes is usually ∼0.315 nm. The thermal vibration is modeled by giving each lattice atom a random displacement (commonly below 0.01 nm). There is an initial random position in the initial orthogonal plane of the SWCNT (or its rope) for each incident ion. Evidently, the initial random positions of all incident ions show the initial beam size. As pointed out by a reviewer, the first-principles calculations could give a more reliable result. Therefore, at present we pay attention to the (nonrelaxed) stationary and dynamic effective potentials for insertion of a dopant into carbon nanotubes, which were found by the preexisting first-principles study.[35]

In this work, the SWCNT is the (30,30) armchair nanotube. Uniform pseudorandom number generators are used to ensure that 98.89 at. % ^{12}C and 1.11 at. % ^{13}C atoms are randomly arranged in the lattice of the SWCNT. For the given system, a

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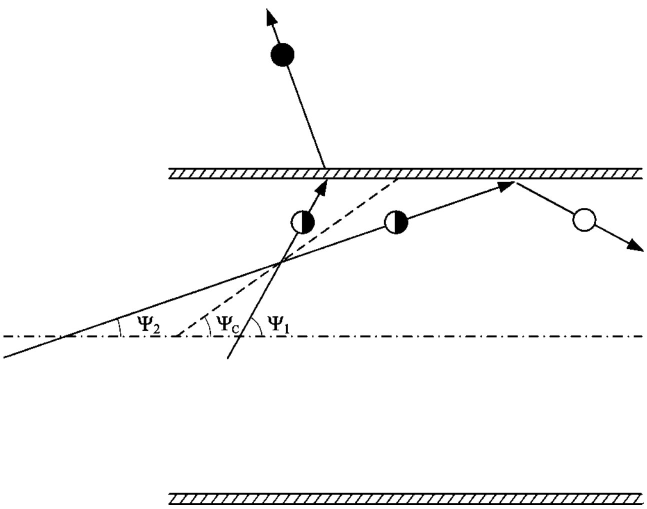

Figure 1. Depiction of the critical angle Ψ_C for an ion beam propagating into the SWCNT. The shaded area represents the single wall. The dashed−dotted line represents the tube axis. Half-filled circles represent incident ions. The hollow circle represents the channeled ion. The filled circle represents the dechanneled ion. Ψ_1 and Ψ_2 are incident angles.

run consists of an incident ^{12}C (or ^{13}C) ion entering a new "undamaged" SWCNT, so zero-fluence propagation into it should be realized.

Two simulation methods[11−13,25,30] can determine the channeling critical angles. The first method calculates the probability of dechanneling (the number of dechanneled ions per incident ion) as a function of incident energy[11] (or angle[25]). There is a detailed explanation of the first method[25] below.

Figure 1 shows the critical angle Ψ_C for the ion beam propagating into the SWCNT. After the incident ion collides with lattice atoms in the single wall, if the incident angle $\Psi > \Psi_C$, it will penetrate through the wall and become the dechanneled ion outside the SWCNT; if the incident angle $\Psi < \Psi_C$, it will be back-scattered from the wall and become the channeled ion inside the SWCNT.

How can we determine Ψ_C in relation between incident angle Ψ and dechanneling probability for a given incident energy? If $\Psi < \Psi_C$, the dechanneling probability approximates 0%. If $\Psi > \Psi_C$, the dechanneling probability rapidly reaches 100%. Therefore, Ψ_C can be determined by a sharp change between dechanneling probabilities, i.e., 0 and 100%.[25]

In general, there are 1×10^3 incident ions in simulating dechanneling probability data.[25] Because the mass deference between ^{12}C and ^{13}C ions is very small, for better accuracy, statistics need to be 1×10^5 in simulating the data in this work.

3. Results and Discussion

It is noteworthy that the channeling is primarily discovered as a result of computer simulations of ion beam propagation along atomic rows in a crystal, based on binary collisions of ions with atoms.[36] After the experimental evidence of the channeling had been established, Lindhard gave a simple theoretical explanation of the channeling; i.e., if the ion enters a single crystal at a sufficiently small angle with respect to an atomic row (or string), it is governed by the transverse continuum potential of the string.[26−28] According to the conservation of the transverse energy, i.e., the transverse incident energy $E\Psi_C^2$ may be equal to $U(R_C)$ [note that $\Psi_C = \sin(\Psi_C)$], he showed the Ψ_C equation to be

$$\psi_C = [U(R_C)/E]^{1/2} \tag{1}$$

where $U(R_C)$ is the channeled ion potential energy at the critical approach distance, R_C. Furthermore, he deduced the $U(R_C)$ equation as follows

$$U(R_C) = 2Z_1Z_2e^2/d \tag{2}$$

where $|Z_1e|$, $|Z_2e|$, and d are the charge of the nucleus of the ion, the charge of the lattice atom, and the distance between atoms in the string (or row), respectively. Although a later theory[28,29] introduced the continuum potential of the atomic plane, instead of that of the atomic row, eq 1 is still of limited validity. This seems to us that as shown in eq 1, in calculation of the channeling critical angle Ψ_C, the theories might consider only the conservation of transverse energy but not that of transverse momentum. In other words, the theories might consider only the transverse energy transfer between the channeled ion and the atomic row (or string) but not their transverse momentum transfer.

In our recent MC simulation works,[30] natural Ar ions and pseudo-Ar ions, i.e., Ar, ^{He}Ar, ^{Ne}Ar, ^{Kr}Ar, ^{Xe}Ar, and ^{Rn}Ar ions (Table 1 of ref 30), have been used to focus the ion mass effect on the channeling critical angle Ψ_C, for the (16,5) SWCNT. Compared with the natural Ar ion, the pseudo-Ar ion (^{He}Ar, ^{Ne}Ar, ^{Kr}Ar, ^{Xe}Ar, or ^{Rn}Ar) has the same nuclear charge but a different mass. For the low-energy channeling of natural Ar ions and pseudo-Ar ions in the (16,5) SWCNT, ref 30 includes the following Ψ_C fitting equation:

$$\psi_C = 51[(M_2/M_1)/E]^{1/2} \tag{3}$$

where E is the incident energy (kiloelectronvolts), M_1 is the ion mass (atomic mass units), and M_2 is the carbon atom mass (atomic mass units).

As shown in eq 3, the channeling Ψ_C critical angles might obey $E^{-1/2}$ and $M_1^{-1/2}$ rules, for the low-energy channeling of natural Ar ions and pseudo-Ar ions in the (16,5) SWCNT. Thus, the question of whether the Ψ_C might obey $E^{-1/2}$ and $M_1^{-1/2}$ rules arises, for the channeling of isotopic ^{12}C and ^{13}C ions in the (30,30) SWCNT. This is a goal of our work.

In Figure 2, in the (30,30) SWCNT, $\Psi_C = (21.3 \pm 0.3)E^{-1/2}$ for the channeling of isotopic ^{12}C ions and $\Psi_C = (20.2 \pm 0.3)E^{-1/2}$ for the channeling of isotopic ^{13}C ions. This means that $(\Psi_{C\ \mathrm{for}\ ^{12}C}/\Psi_{C\ \mathrm{for}\ ^{13}C}) = (21.3/20.2) = (13/12)^{1/2}$. In other words, Ψ_C might obey $E^{-1/2}$ and $M_1^{-1/2}$ rules, for the channeling of isotopic ^{12}C and ^{13}C ions in the (30,30) SWCNT.

As mentioned above, according to the conservation of transverse energy, i.e., the transverse incident energy $E\Psi_C^2$ may be equal to $U(R_C)$ [note that $\Psi_C = \sin(\Psi_C)$], Lindhard has shown $\Psi_C = [U(R_C)/E]^{1/2}$.[26,27] Reference 11 has suggested that $\Psi_C = [U(R_C)/E]^{1/2}$ can be rewritten as $\Psi_C = C(E)^{-1/2}$ [note that C is corrected with $U(R_C)$]. Our recent work[25] has suggested that as one explanation of the incident momentum influence, C is correlated not only with $U(R_C)$ but also with ion mass M_1. At present, we emphasize that the low-energy ion channeling should obey both the transverse energy and transverse momentum conservations. $E\Psi_C^2$ is the conserved transverse energy, and $(2M_1E)^{1/2}\Psi_C$ is the conserved transverse momentum. Because $E\Psi_C^2$ equals one constant, $\Psi_C = C(E)^{-1/2}$ as shown in ref 11. Also, because $(2M_1E)^{1/2}\Psi_C$ equals another constant, in our opinion, $\Psi_C = C_1(M_1E)^{-1/2}$, where C and C_1 are constants. This is why Ψ_C might obey $E^{-1/2}$ and $M_1^{-1/2}$ rules, for the channeling of isotopic ^{12}C and ^{13}C ions in the (30,30) SWCNT.

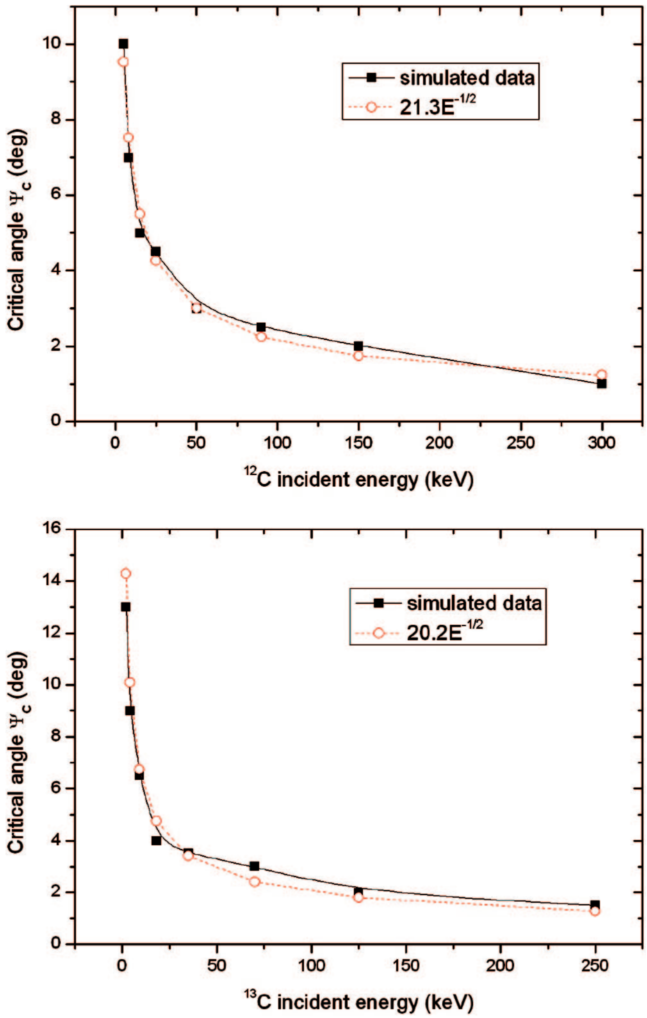

Figure 2. Channeling Ψ_C critical angle as a function of ^{12}C and ^{13}C incident energies for the (30,30) SWCNT.

Interestingly, it is found in MD simulations that $U(R_C) = 450$ eV and $\Psi_C = (450\ \text{eV}/E)^{1/2}$ for Ar ion channeling[11] and $U(R_C) = 500$ eV and $\Psi_C = (500\ \text{eV}/E)^{1/2}$ for carbon ion channeling,[12] if a Ψ_C of $[U(R_C)/E]^{1/2}$ is suggested. Namely, the relationship $\Psi_{C,\text{for Ar ion channeling}}/\Psi_{C,\text{for carbon ion channeling}} = (450/500)^{1/2}$ in MD simulations works.[11,12] However, $\Psi_{C,\text{for Ar ion channeling}}/\Psi_{C,\text{for carbon ion channeling}} = (18/6)^{1/2}$ in the theory (eqs 1 and 2), because $Z_1 = 6$ for the carbon ion and $Z_1 = 18$ for the Ar ion, where $|Z_1e|$ is the nucleus charge of the ion. What can produce this critical angle difference between the MD simulation works and the theory? The ion mass M_1 effect is the negative one on Ψ_C; i.e., Ψ_C decreases as M_1 increases.[25]However, the ion nucleus charge effect ($|Z_1e|$) is the positive one on Ψ_C; i.e., Ψ_C increases as Z_1 increases (eqs 1 and 2). Thus, the relationship $\Psi_{C,\text{for Ar ion channeling}}/\Psi_{C,\text{for carbon ion channeling}} = (18/6)^{1/2}$ becomes $\Psi_{C,\text{for Ar ion channeling}}/\Psi_{C,\text{for carbon ion channeling}} = (450/500)^{1/2}$, because $Z_1 = 6-18$ and $M_1 = 12-39.9$ amu, i.e., mainly because the ion mass effect reduces the ion nucleus charge one on critical angle Ψ_C.

4. Summary

Monte Carlo (MC) simulation studies of isotopic mass effects have been conducted, for low-energy channeling of ^{12}C and ^{13}C ions in single-wall carbon nanotubes. Uniform pseudorandom number generators are used to ensure that 98.89 at. % ^{12}C and 1.11 at. % ^{13}C atoms are randomly arranged in the lattice of the SWCNT. For a given system, a run consists of an incident ^{12}C (or ^{13}C) ion entering into a new "undamaged" SWCNT, so zero-fluence propagation into it should be realized.

It is found in MC simulations that $(\Psi_{C\ \text{for}\ ^{12}C}/\Psi_{C\ \text{for}\ ^{13}C}) = (13/12)^{1/2}$, for the same incident energies. The reason for this may be that $(2M_1E)^{1/2}\Psi_C$ is the conserved transverse momentum.

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