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Low energy ion scattering in He/HOPG system

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Abstract

Low energy ion scattering (LEIS) is a unique tool in surface analysis, since it provides the atomic composition of the outer atomic layer, and time of flight ion scattering (TOF) is a non-destructive method of analysis that is sensitive to all elements. The outer surface atoms dominate many processes such as adhesion, electron emission, growth, wetting and overall catalysis. In catalysis, LEIS applications include understanding and improvement of catalytic phenomena, site of poisoning, size of nanoclusters and quantification of promoters.

In this work, we study the neutralization of low energy He^+ ions on graphite (highly oriented pyrolytic graphite, HOPG) verifying that the ion fraction is close to null, i.e., a large neutralization probability. Resonant neutralization to the ground state (RN) has been the main mechanism expected for He^+ scattered by HOPG, but we found that only by including the resonant neutralization to the first excited state (1s, 2s), the small ion fractions measured can be explained.

Keywords: LEIS; Catalysis; HOPG; Resonant neutralization

1. Introduction

Low energy ion scattering (LEIS) is an analytical tool that provides information on the atomic composition of the outer surface. Thus, quantitative composition analysis is currently done on a huge variety of materials, including catalysis and organic materials [1].

In the early 1960s, Panin [2], and Walther and Hintenberger [3] demonstrated that for inert gas ions a clear correlation exists between the energy loss of a scattered ion and the identity of the surface atoms. In 1967 the work of Smith [4,5] gave strong impulse to the use of low energy spectra of scattered ions for composition analysis. On the other hand, shadowing and blocking effects enables the use of angular dependent studies to determine the location of surface atoms on the surface of single crystals. Nowadays LEIS is usually applied to conductors, insulators, atomically flat single crystals as well as highly dispersed amorphous materials [6]. In addition to the exploitation of the surface sensitivity, it is also possible to obtain in depth information on the composition of the outer few nm [1,6] by adding sputter depth profiling. Since the early 1990s, the introduction of time of flight (TOF) methods gave place to the development of time of flight scattering and recoiling spectrometry (TOF-SARS) as a tool for structural analysis [7,8]. This improvement provided a LEIS spectroscopy that it is sensitive to all elements, allowing the determination of surface and adsorbate structures to an accuracy of up to 0.1 Å.

Nowadays typical applications include:

Adhesion: origin of pinholes in thin layers, improvement of primers.
Wetting: development of new anti-wetting surfaces.
Biology/medicine: biocompatibility, biosensors, bone growth.
Semiconductors: thickness distribution, high *k*-dielectrics, diffusion barriers.
Electron emission: understanding low work function materials, development of new cathodes.
Catalysis: understanding and improvement of catalytic phenomena [9,10], site of poisoning, size of nanoclusters and quantification of promoters.

Although significant progress has recently been made in the understanding of the underlying charge exchange processes, it is

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an intriguing reality that the charge exchange processes in LEIS are not fully understood.

In this work, we present measurements of low energy (5 keV) He^+ ion scattering neutralization probabilities from highly oriented pyrolitic graphite (HOPG) for a couple of scattering angles in specular conditions. We also present a quantum mechanical calculation that takes into account, in a correlated way, the neutralization to He ground and excited states in He^+/HOPG collisions.

2. Experimental

LEIS experiments were performed in a UHV VARIAN chamber, with a base pressure of 10^{-9} Torr, and equipped with an ion gun, that includes a Colutron ion source, focusing lens, a Wien filter and pulsing plates. Two TOF tubes are attached to the chamber, one in the backscattering direction (135° scattering angle) and the other in the forward direction (45° scattering angle). The HOPG sample was cleaned in UHV by annealing at 1300 K for several minutes. In order to perform the TOF measurement a pulsed ion beam was generated. The ion pulsed current was ~80 pA. The scattered projectiles were detected by a channeltron multiplier. Deflection plates located at the TOF tube entrance allow to separate ions from neutrals.

In the experiments we use 5 keV He^+ ions. The ingoing/outgoing angles were selected to be equals (specular conditions); 22.5° (forward direction) and 67.5° (backscattering direction) measured with respect to the HOPG surface plane.

TOF spectra for total (neutrals plus ions) and only neutral particles were recorded using a multiple-stop time spectrometer (Ortec MCS-plus). To estimate the neutralization probability of ions scattered elastically from the HOPG surface we select a narrow TOF interval, 160 ns ($\Delta E \cong 400$ eV) in forward scattering and 200 ns ($\Delta E \cong 120$ eV) in backscattering, close to the high energy onset of the peaks. Experimental errors were estimated from the statistical error of various experiments.

3. Theory

The inclusion of the ground and first excited states as possible final charge configurations requires an appropriate calculation where only one electron transference (either to the He1s or to the He2s) is allowed, inhibiting the He negative charge configuration. This kind of calculation is achieved by using a developed formalism based on the infinite-correlation approach to the Anderson Hamiltonian [11]. In a simplified picture, by considering the spin component of the first electron in He^+ frozen, a second electron with the same spin component is responsible for the neutralization to the excited state (1s↑2s↑), while a second electron with the opposite spin component is responsible of the neutralization to the ground state (1s↑2s↓). The Hamiltonian can be written as:

$$H=\sum_{k,\sigma}\varepsilon_k n_{k\sigma}+\sum_{\sigma}E_\sigma n_\sigma+\sum_{k,\sigma}\left[V_{k\sigma}c^+_{k\sigma}b^+c_\sigma+hc\right]$$

here k denotes the solid band states (the valence and the core ones) with energy values ε_k, and $c^+_{k\sigma}$ creates an electron in a band state of the solid with spin projection σ. The operator c_σ destroys an electron either in the 1s ($\sigma=\downarrow$) or 2s ($\sigma=\uparrow$) states of He; the energies, corresponding to the 1s and 2s neutralization channels, are defined as total energy differences:

$$E_\uparrow=E_{\text{tot}}(1\text{s}^1 2\text{s}^1)-E_{\text{tot}}(1\text{s}^1)$$
$$E_\downarrow=E_{\text{tot}}(1\text{s}^2)-E_{\text{tot}}(1\text{s}^1)$$

in this form $\langle n_\sigma\rangle$ gives the He ground state configuration probability for $\sigma=\downarrow$ and the He excited state configuration probability for $\sigma=\uparrow$.

The boson operator $b^+(b)$ ensures the projection on the correct subspace through the constraint relation,

$$b^+b+\sum_{\sigma}n_\sigma=1;$$

3.1. Calculation of the neutralization probabilities

The average occupations are calculated by using the expression:

$$\frac{\mathrm{d}\,\langle n_\sigma(t)\rangle}{\mathrm{d}t}=2Im\sum_{k}V_{\sigma k}(t)\left\langle c^+_\sigma b c_{k\sigma}\right\rangle_t$$

with the crossed term given by:

$$\left\langle c^+_\sigma b c_{k\sigma}\right\rangle_t=-\frac{1}{2}\int_{t_0}^{t}\mathrm{d}\tau V_{k\sigma}(\tau)\{F_{\sigma\sigma}(\tau,t)\\ -[2f_<(\varepsilon_k)-1]G_{\sigma\sigma}(\tau,t)\}\exp[i\varepsilon_k(\tau-t)]$$

here $f_<(\varepsilon_k)$is the Fermi distribution. The Green functions,

$$G_{\sigma\sigma}(t,t')=i\Theta(t'-t)\left\langle\{c^+_\sigma(t')b(t'),b^+(t)c_\sigma(t)\}\right\rangle$$
$$F_{\sigma\sigma}(t,t')=i\left\langle[c^+_\sigma(t')b(t'),b^+(t)c_\sigma(t)]\right\rangle$$

are solved for the case of two non-degenerate states by following the procedure of Ref. [11] based on the method of motion equations.

By using a LCAO expansion of the solid states (k), we can write finally:

$$\frac{\mathrm{d}\,\langle n_\sigma\rangle}{\mathrm{d}t}=-Im\sum_{i,j,R_\text{s}}\int_{-\infty}^{\infty}\mathrm{d}\varepsilon\rho_{i,j}(\varepsilon)V_{\sigma,iR_\text{s}}(t)\\ \times\int_{t_0}^{t}\mathrm{d}\tau V_{jR_\text{s},\sigma}(\tau)\{F_{\sigma\sigma}(\tau,t)\\ -[2f_<(\varepsilon)-1]G_{\sigma\sigma}(\tau,t)\}\exp[i\varepsilon(\tau-t)]$$

where the indexes i, j refer to the states of the surface atom centered at position R_s, and $\rho_{i,j}(\varepsilon)$ is the surface local density of states (LDOS) of HOPG [12,13].

The atom–atom hopping terms $V_{j\sigma}$ are obtained from a bond-pair model of the atom–surface interaction [14], by using Gaussian-type functions for describing the states of helium (1s, 2s) and of carbon (1s, 2s, 2p) [15]. Normal ion trajectories and the interaction with only one atom of the surface are considered, and the turning points are calculated from the helium–carbon interaction energy. The translational factors accounting for the parallel velocity effects are expected to be important for near