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A New Analytical Method in Surface Electron Spectroscopy: Reverse Monte Carlo Method*

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A reverse Monte Carlo (RMC) method is developed in this work to study the energy-loss process of signal electrons in surface electron spectroscopy. This method derives the effective energy-loss function (EELF) from a measured reflection electron energy loss spectroscopy (REELS) spectrum by an iterative Monte Carlo (MC) simulation procedure other than deconvolution procedure, in accordance with the complicated electron transport process. The method combines the Markov chain Monte Carlo (MCMC) sampling (i.e. Metropolis important sampling) of oscillator parameters with a usual MC simulation of electron interaction with solids, which acts as a single step of MCMC sampling. To examine the reliability of this method, we have performed a test which leads to derive the same EELF with different trial inputs of initial oscillator parameters. Calculation results show that EELF can be pretty well derived by the RMC method even without a proper choice of initial trial parameters. As an example the EELFs for Ag at different electron energies are derived from the measured REELS spectra by this RMS method.
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Keywords: Reverse Monte Carlo; REELS; Effective energy-loss function; Silver

I. INTRODUCTION

Precise information of optical properties for various surface nanostructures or ultrathin films is becoming more important to material science. However, it is difficult to measure the optical data by optical methods for specific nanostructured materials. Fortunately, such information is essentially contained in, and therefore, may be extracted from surface electron spectroscopy spectra, like reflection electron energy loss spectroscopy (REELS) spectra, due to shorter information depth of signal electrons compared with that of photons. The optical property of the sample is related with electron inelastic interaction during signal production process. But, the interaction of electrons with a surface is generally quite complex since different types of collisions occur along electron trajectories. In addition to elastic scattering, typical inelastic scattering mechanism includes bulk and surface excitations, interband and intraband transitions. Furthermore, multiple scattering effect presents because the relevant mean free paths for electron scattering channel is compared with or even shorter than the structure size. Hence, derivation of optical data from the REELS spectra requires removing the elastic scattering and multiple scattering effects in analysis.

The question then arises how to extract the single scattering loss distribution from an experimental spectrum. Tougaard and Chorkendorff [1] had presented a simple deconvolution formula while the physical model is based on a so-called P1-approximation, in which the expansion of the elastic scattering cross-section in spherical harmonics is terminated after the first order [2]. In the medium energy region, the higher order phase shifts are by no means negligible [3] and consequently the P1-approximation does not provide a good physical basis to model REELS spectra. A deconvolution procedure for REELS spectra [4–6], is then introduced by several authors independently, in which elastic scattering is treated more realistically. Although this provides a better model to describe REELS spectra, the resulting deconvolution procedure leads to results that are quite similar to those by using the Tougaard and Chorkendorff's algorithm, due to the neglect of surface excitations in this procedure.

Yoshikawa *et al.* [7–9] have derived the EELF from an analysis of the REELS spectrum by the Landau formulation with incorporation of a Monte Carlo (MC) simulation of electron trajectories. By applying this method, named extended Landau formulation or the extended Landau approach [10], Shimizu and coworkers [11–14] derived the EELF and verified them by reproducing the REELS spectrum by performing MC simulations based on the use of the relevant EELF instead of the optical energy loss function (ELF) used in conventional MC simulations [15, 16]. However, there still has been a discrepancy between reproduced and experimental data.

Recently, Werner has presented a procedure to decompose experimental REELS spectra of medium-energy electrons reflected from solid surfaces into contributions due to surface and bulk electronic excitations [17, 18]. The procedure is based on the simultaneous deconvolution of a set of two REELS spectra taken at different energies or geometrical configurations for which the relative contribution of surface excitation to bulk excitation differs substantially. The main assumption in this procedure is that the surface and bulk excitations for electron inelastic scattering can be treated as separate events [19]. Recently, an example was published for Au where two sets of REELS spectra taken at different energies above 1000 eV, where the influence of the surface is less critical, were shown to give similar results [20]. However, for use of REELS to study the dielectric properties of nanostructures or ultrathin films it is necessary to consider low primary electron energy.

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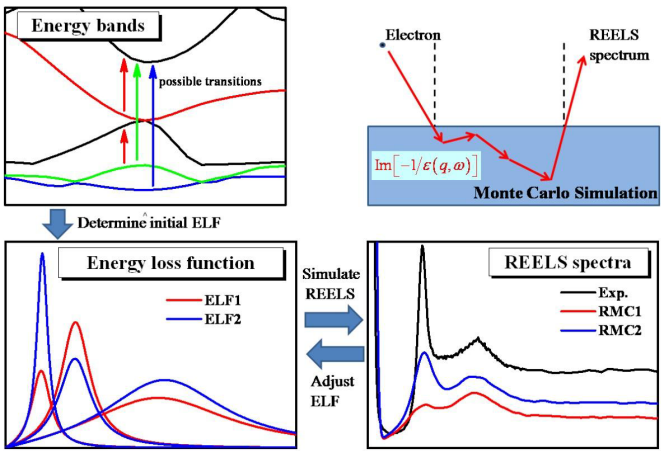

FIG. 1: Diagram of a simplified process of forming a REELS spectrum, Monte Carlo process and a schematic diagram of RMC process to deduce the effective ELF form a measured REELS spectrum.

Due to complicated electron transport process, ELF is involved in the measured spectrum in a complex way other than a simple convolution. Therefore, it is very difficult to find a suitable mathematical formalism to obtain the desired optical data from a measured spectrum. In the present work, we have developed a new method, the reverse Monte Carlo (RMC) method, to deduce EELF efficiently. This method is in principle based on an iterative process: an initial EELF is determined by the oscillator parameters which may be chosen from the calculated band structure and total density of states (DOS). This test EELF is then employed in a MC simulation of electron interaction with sample to estimate the accuracy of oscillator parameters by comparing the simulated REELS spectrum with an experimental spectrum; according to the difference the EELF is updated by modifying oscillator parameters, and the process is repeated until the difference is negligible. The complicated electron transport process approached by the MC simulation instead of analytical deconvolution procedure is the most suitable method to deal with electron-solid interaction. In this method, it is important to minimize the computation by using Markov chain Monte Carlo (MCMC) sampling to adjust a good deal of oscillator parameters. Comparison of the calculations with different initial EELF as inputs for Ag sample shows that the EELF can be reasonably derived by the RMC method. The EELFs of Ag sample for different primary electron energies are also presented by the RMC method.

II. THEORETICAL METHODS

The RMC method developed in this work to deduce EELF from measured REELS data is an iterative MC simulation process as shown in Fig. 1, in which each iterative step, i.e. a new MC simulation of REELS spectrum, is performed with newly updated oscillator parameters for calculation of inelastic scattering cross-section with this EELF. An initial EELF can be arbitrarily determined, but, may also be determined by the calculated band structure and total DOS for faster convergence. Then this test EELF is employed in a MC simulation of electron interaction with sample to estimate its accuracy by comparing the simulated REELS spectrum with an experimental spectrum. According to the difference the EELF is updated according to MCMC method to obtain most appropriate oscillator parameters in an efficient way. In other words, the principle of RMC method is to choose efficiently the best fitted EELF, which reproduces MC simulated REELS spectrum with the smallest discrepancy to the measured spectrum, from a large number of trial EELFs

A. Physical model for MC simulation

The main features of the physical model for MC simulation to produce REELS spectrum in this work is based on the use of Mott cross section in describing electron elastic scattering and a dielectric approach to electron inelastic scattering.

The relativistic expression of electron-atom scattering, the Mott differential cross section [21], is given by

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |g(\theta)|^2 \tag{1}$$

with the scattering amplitudes calculated by the partial wave expansion method [22],

$$\begin{aligned} f(\theta) &= \frac{1}{2iK}\sum_{l=0}^{\infty}\left\{(l+1)(2e^{2i\delta_l^+}-1)+l(e^{2i\delta_l^-})\right\}P_l(\cos\theta); \\ g(\theta) &= \frac{1}{2iK}\sum_{l=0}^{\infty}\left\{e^{2i\delta_l^+}+e^{2i\delta_l^-}\right\}P_l^1(\cos\theta). \end{aligned} \tag{2}$$

In the above equation $P_l(\cos\theta)$ and $P_l^1(\cos\theta)$ are, respectively, the Legendre and the first-order associated Legendre functions. δ_l^+ and δ_l^- are spin-up and spin-down phase shifts of the l-th partial wave. The phase shifts are numerically evaluated by solving the Dirac equation for the radial part of the wave function of the scattered electron. The Thomas-Fermi-Dirac atomic potential [23] is used in the calculation.

The differential cross section for electron inelastic scattering in a solid is represented in dielectric theory in terms of ELF, $\mathrm{Im}\{-1/\varepsilon(q,\omega)\}$, as

$$\frac{d^2\lambda_{\mathrm{in}}^{-1}}{d(\hbar\omega)dq} = \frac{1}{\pi a_0 E}\mathrm{Im}\left\{\frac{-1}{\varepsilon(q,\omega)}\right\}\frac{1}{q}, \tag{3}$$

where $\hbar\omega$ and $\hbar q$ are the energy loss and the momentum transfer, respectively, from an electron of kinetic energy E penetrating into a solid of dielectric function, $\varepsilon(q,\omega)$. λ_{in} is the electron inelastic mean free path. ELF may be derived from optical constant database in plasmon-pole approximation [24] or according to Ritchie and Howie's scheme [25], in which an extrapolation from the optical limit ($q = 0$) to other momentum transfers was made: ELF $\mathrm{Im}\{-1/\varepsilon(q,\omega)\}$ is approximately extended from an optical ELF, $\mathrm{Im}\{-1/\varepsilon(\omega)\}$. ELF is firstly decomposed into N-terms of the Drude-Lindhard model ELF:

$$\mathrm{Im}\left\{\frac{-1}{\varepsilon(q,\omega)}\right\} = \sum_{l=1}^{N} a_i \mathrm{Im}\left\{\frac{-1}{\varepsilon(q,\omega;\omega_{pi},\gamma_i)}\right\}, \tag{4}$$

where the $3N$ oscillator parameters, a_i, γ_i and ω_{pi} are, respectively, the oscillator strength, energy and width of the i-th oscillator. In this work the optical ELF, instead of by using the database of optical constants, is constructed by given values of oscillator parameters.

B. Algorithm of MCMC procedure

The iterative process RMC uses a standard MCMC procedure [26] to update these oscillator parameters efficiently. The algorithm for this process is therefore as follows:

1) Initial $3N$ oscillator parameters can be arbitrary positive figures, but this would require much longer convergence time. One may start with parameters partly deduced from first-principles calculation: initial parameters, a_i and γ_i, are simply generated at random while the initial ω_{pi} parameters are determined from the calculated energy bands and total DOS.

2) Based on this old ELF, a Monte Carlo simulation is performed to obtain the REELS spectrum $I_0^{\rm sim}(\Delta E_j)$ where the index j denotes the j-th experimental grid value of energy loss ΔE.

3) Calculate standard deviation between the experimental REELS spectrum, $I^{\rm exp}(\Delta E_j)$, and the MC simulated spectrum, $I_0^{\rm sim}(\Delta E_j)$:

$$\chi_0^2 = \sum_j \left(I_0^{\rm sim}(\Delta E_j) - I^{\rm exp}(\Delta E_j)\right)^2 / \sigma(\Delta E_j)^2, \qquad (5)$$

where the summation is taken over the experimental grid values of energy loss, and $\sigma(\Delta E)$ is the artificially specified weighted factor to make this process more efficient.

4) Move one oscillator parameter, such as strength, energy or width of oscillator, at random. Then calculate the new ELF, and perform a new simulation of REELS spectrum to derive $I_1^{\rm sim}(\Delta E_j)$. This produces a new standard deviation,

$$\chi_1^2 = \sum_j \left(I_1^{\rm sim}(\Delta E_j) - I^{\rm exp}(\Delta E_j)\right)^2 / \sigma(\Delta E_j)^2. \qquad (6)$$

5) Calculate $\Delta\chi_1^2 = \chi_1^2 - \chi_0^2$. If $\Delta\chi_1^2 < 0$, the move is accepted and this new ELF becomes the old ELF for next iteration. If $\Delta\chi_1^2 > 0$, then the move is accepted with the probability, $\exp(-\chi_1^2)/\exp(-\chi_0^2) = \exp\{-(\chi_1^2-\chi_0^2)\}$; otherwise, it is rejected and the old ELF is remain unchanged, according to Metropolis importance sampling [27, 28].

6) Repeat step-4 for next iteration to calculate $\Delta\chi_2^2 = \chi_2^2 - \chi_1^2$. Successive iteration generates decreasing χ_n^2 until it reaches an equilibrium value for converging $\Delta\chi_n^2$ within an acceptable error, with which oscillator parameters best describe experimental REELS spectrum, with slight fluctuation.

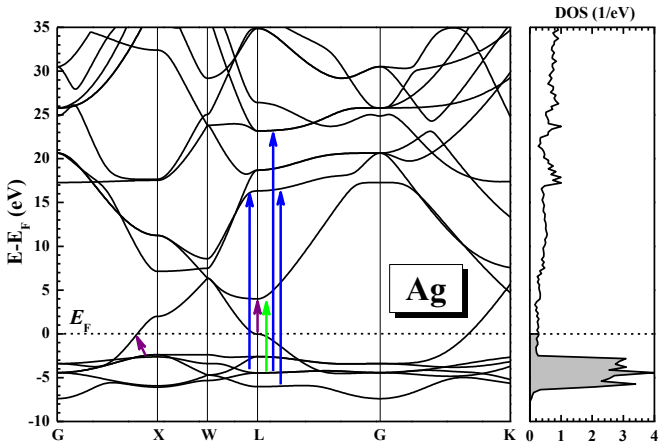

FIG. 2: Calculated band structure (left) and total DOS (right) of bulk silver in the energy range −10 to 35 eV. The Fermi energy is set to zero.

This procedure can easily and automatically optimize the EELF to the smallest difference between the simulated and measured data. It is particularly important that this RMC uses a MCMC principle to accelerate the global optimization of $3N$ oscillator parameters to reach minimum "potential" curve, χ^2, in $3N$-dimension. The final results should be independent of the initial inputs for parameters.

III. RESULTS AND DISCUSSIONS

The calculated band structure and total DOS of bulk FCC Ag in energy rang −10 to 35 eV is presented in Fig. 2. The occupied states are composed of a very broad band from *sp* states, and a much narrower band corresponding to 4*d* states. The latter ranges from −6.2 to −2.8 eV below the Fermi level $E_{\rm F}$. In contrast to occupied states, the total DOS exhibits less pronounced features above the Fermi level. However, oscillations in the DOS are not artifacts of the calculation, but are rather van-Hove type (pseudo) singularities, originating from flat bands at high-symmetry points. Some of the possible transitions from occupied bands into unoccupied bands are also draw in Fig. 2. From various possible excitations, the energy of initial oscillators is determined at first to improve the convergence of RMC process, then strength and width of oscillators are given randomly. For Ag, the energy of nine oscillators is chosen as, 3.4, 3.9, 7.4, 9.2, 16.3, 24.1, 30.3, 44.7 and 53.2 eV.

Using these initial oscillator parameters, the RMC procedure is performed for Ag and at electron energy of 500 eV; the incident angle is 50° and the detection is at the surface normal direction with solid angles of 12°. Figure 3 shows the updating of these oscillators in the RMC process in order to reduce the difference on REELS spectrum between the experiment and simulation. The changing of the EELF and the normalized standard deviation χ^2 with the iteration MCMC step are shown in Fig. 4 in detail. It is seen that the deviation χ^2 becomes stable after about 1000 accepted MCMC steps. It is found that the obtained EELF becomes consistent within a maximum error of 0.037 after about 3000 accepted MCMC steps, espe-

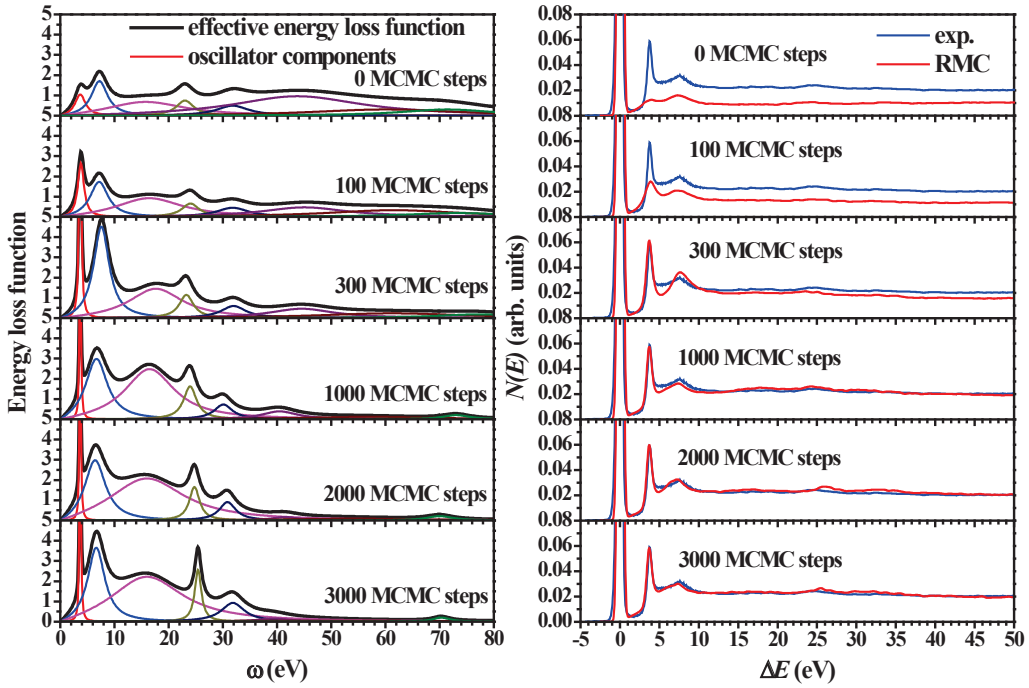

FIG. 3: The updating process of oscillator parameters in the RMC process to derive ELF (left) and REELS spectrum in comparison with experimental spectrum (right).

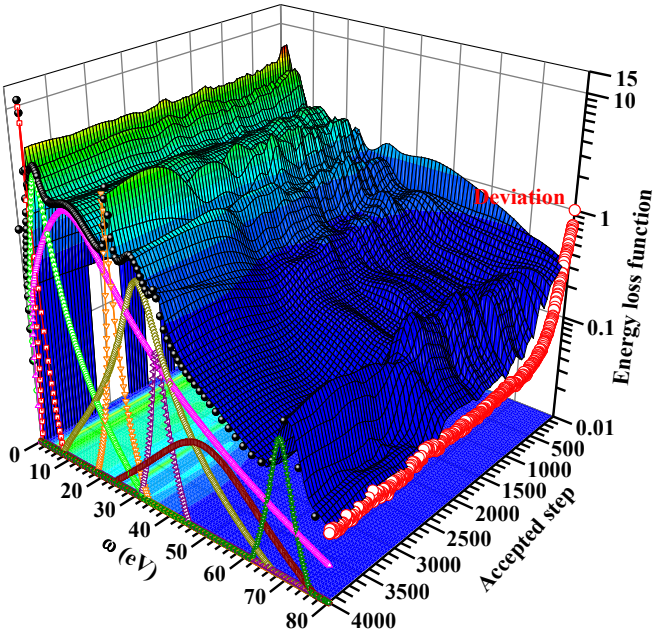

FIG. 4: A plot of EELF contributed by first eight oscillators together with the normalized standard deviation (red open circle) with the accepted MCMC steps.

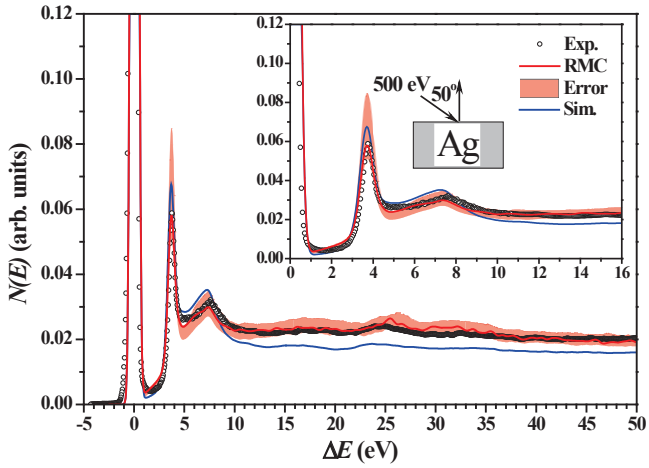

FIG. 5: The comparison of the final simulated REELS spectrum (red curve) together with the error range (red area) with experiment (black circle) and another direct simulation of REELS spectrum including surface excitation (blue curve).

cially for the oscillators in low energy loss region. Figure 5 shows the final simulated REELS spectrum together with the error range, which is determined by the maximum and the minimum values of obtained EELFs in every accepted steps when the deviation becomes stable after about 1000 accepted steps. For comparison, another direct simulation of REELS spectrum by our previous Monte Carlo method [29] which includes surface excitation in electron inelastic scattering [30, 31] by using optical constants is also shown. It is obviously that the final obtained REELS spectrum agrees with measured one better than the spectrum simulated in our previous work [32], and the measured spectrum is within the error range of the present MC simulation using the EELF in MCMC process.

In order to ensure the reliability of the RMC method, we have also performed a test in which different initial EELFs are used but with the same experimental REELS spectrum. Figure 6 shows uncertainty range calculated by the maximum and the minimum values of eight different

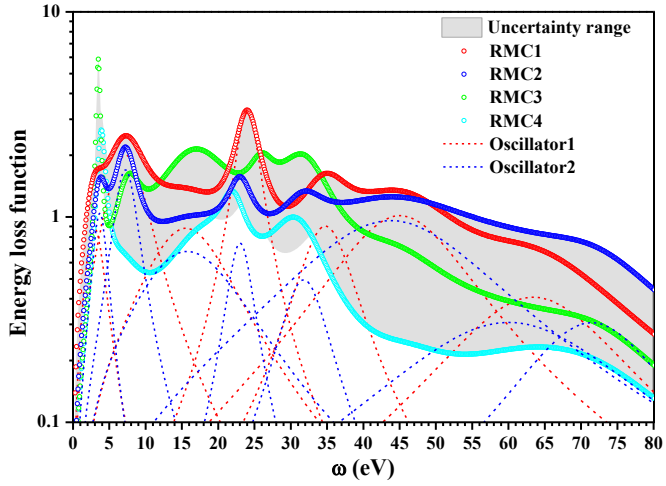

FIG. 6: A plot of uncertainty range of eight different initial EELFs (gray area), four initial EELFs (open square) and components of oscillators (red and blue dashed lines) for two EELFS.

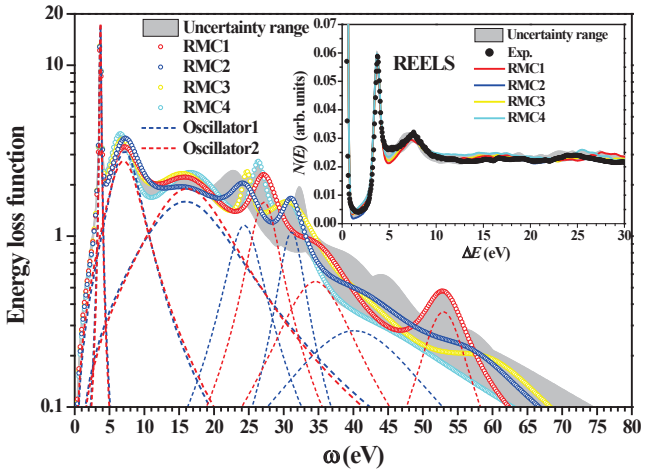

FIG. 7: A plot of uncertainty range (gray area) of eight different final EELFs after RMC process, four final EELFs (open square) corresponding to the initial EELFs in Fig. 6 and components of oscillators (red and blue dashed lines) for two EELFS. The inset is uncertainty range of corresponding final simulated REELS spectra (gray area) together with four corresponding spectra (curve).

initial EELFs together with four different initial EELFs as example. The oscillator parameters of these trial EELFs are given randomly. By input these initial EELFs in RMC processes, the output EELFs and the relevant final MC simulated REELS spectrum together with the error range are shown in Fig. 7. All these obtained REELS spectra from RMC procedure agree well with experimental spectrum. It is obviously that all the obtained EELFs with different inputs do converge after the deviation becomes stabilized and the consistence is found excellent in the low energy loss region due to the smaller influence of multiple inelastic scatterings. These results prove that the final results are independent of the initial trial inputs; this is obviously the property of Markov chain used in RMC method. It also ensures that the EELFs can be reasonably derived by this RMC method even without a proper choice of initial oscillator parameters.

IV. CONCLUSIONS

In conclusion, a new theoretical method, the reverse Monte Carlo (RMC) method, is developed to deduce EELF efficiently. The method is constituted of MCMC sampling of oscillator parameters for deriving EELF used in MC simulation of REELS spectrum to agree with experimental spectrum. The obtained EELF by RMC method is independent of the initial oscillator parameters for trial input of EELF. This RMC method is a successful method for studying the energy-loss processes of signal electrons not only in REELS but also in other surface electron spectroscopy.

Acknowledgments

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