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Identification of mechanisms of ion induced electron emission by factor analysis

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Abstract

Introducing the use of the Factor Analysis method to analyze electron emission spectra we identify different mechanisms for electron emission from clean Al surfaces under bombardment by Ar^+ and Li^+ ions. The analysis of the energy electron emission distributions and their dependence on incoming ion energy allows separation of the direct contribution of Auger neutralization from that of plasmon de-excitation and cascade electrons due to kinetic emission. Similarly, the analysis shows that, under our experimental conditions, plasmons are excited by fast Al-2p Auger electrons produced in symmetric Al–Al encounters in the atomic collision cascades initiated by the projectiles.
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Electron emission in slow ion–solid interactions is a basic phenomenon that has been studied for decades [1,2]. In spite of substantial research, new basic mechanisms are still being discovered, and exciting experimental results frequently promote new developments, renewed interest and debate [3,4]. The processes leading to electron ejection have been operationally divided in two main classes of excitation mechanisms, leading to *kinetic* and *potential* electron emission. The release of the potential energy of the incoming ion (neutralization energy) can occur either through Auger neutralization or resonant neutralization followed by an Auger de-excitation [1,2], or by plasmon-assisted neutralization followed by its decay in an excited electron [4]. If the neutralization energy is at least twice the work function of the solid, electron ejection is possible by the Auger neutralization or de-excitation mechanisms, whereas plasmon-assisted neutralization requires that the energy released in neutralization equals the energy of a surface plasmon. On the other hand, when the

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origin of the energy consumed by the electron ejection process is the kinetic energy of the impinging ion, the mechanism is known as kinetic emission. A coupling between both mechanisms is also possible, for instance the transformation of kinetic into potential energy, previous to potential emission, due to collisional shifting of the atomic energy levels.

With few exceptions, such as core-excited Auger electrons, ion-induced electron emission involves very low energy electrons. There are several physically meaningful mechanisms that produce such electrons, which are unfortunately shadowed by the continuum spectrum that results from a cascade of inelastic electron-electron collisions (collision cascade) in the solid. Moreover, sometimes electrons with the same characteristic energy may have different origins. A clear example is electron emission from plasmon de-excitation, where the plasmon might be excited directly by the projectile or indirectly by fast secondary electrons [5,6].

Here we apply for the first time Factor Analysis (FA) [7], to extract physical information from ion-induced electron energy spectra. We demonstrate the method with new measurements of electron emission from Al excited by Ar^+ and Li^+ ions in the projectile energy range 1–5 keV. Although Al is one of the most studied targets in electron emission, there is still controversy about the origin of some features concerning the energy spectra. The contrast of Ar^+ and Li^+ is interesting because Ar^+ can excite electrons by the potential and kinetic mechanisms, whereas Li^+, due to its low neutralization energy, can only excite electrons via the kinetic processes. In addition, kinetic emission by these two ions should differ due to differences in mass and electronic structure. We show below how Factor Analysis allows separating the potential and kinetic contributions in the case of Ar^+, demonstrating the kinetic origin of the plasmon excitation in this case. In the case of Li^+, application of FA shows that the electron emission spectra induced by Li^+ originates solely, within the sensitivity of the method, from the kinetic excitation of Aluminum-2p Auger electrons.

The experiments were done in a commercial surface analysis system (Perkin–Elmer SAM 590A) equipped with a cylindrical mirror analyzer.

The base pressure was in the low 10^{-10} Torr. The sample was obtained by evaporation of pure (99.999) Al in UHV. Contamination was monitored by means of Auger Electron Spectroscopy (AES) but, since ion-induced electron emission is quite more sensitive to contamination than AES [4], the ultimate check of the surface state was the repetitiveness of the measured ion-induced electron energy spectra. The ion current density was kept very low, (<20 nA/cm^2) to avoid contamination by ion implantation. Nevertheless, at each energy, several measurements were performed using the same beam position and different positions to test for (and discard) any influence of contamination. At least three series (energy variations) for each projectile on different samples were performed. The sample was electrically biased at −6 V to ensure the acquisition of the complete energy spectra. The incidence angle of the ion beam with respect to the sample normal was 54° for Ar^+ and 60° for Li^+ ions.

As mentioned above, one of the key aspects of this work is the introduction of Factor Analysis as a powerful method to either isolate or identify mechanisms in electron emission. FA is a well-known data reduction procedure to analyze spectra, particularly in physical chemistry. It has been successfully applied to different spectroscopies [7,8] and is currently included as a standard data treatment procedure in most spectroscopy software packages. We will outline the method here and refer the reader to a classic textbook [7] for details. The main ability of FA is to identify linearly independent factors (bases) with which to decompose a series of spectra taken under different conditions (the projectile energy in our case). The first step in FA, known as principal component analysis (PCA), is the determination of the minimum number of such linearly independent factors or pure components. The simple idea behind PCA is that a determinant of any matrix with linearly dependent columns or rows is null. Thus, the key task is to determine the number of eigenvalues which are physically meaningful, given experimental errors, with the aid of several test methods [8]. Once this number is known, each factor, and its weight, is determined through a least square fit procedure, called Target Transformation [7], i.e.

one minimizes the quadratic difference between the experimental spectra and that constructed from the linear combination of the factors. We note here that this procedure does not handle continuously variable spectral shape, such as, i.e., peak broadening by the Doppler effect [2], although in principle it is still possible to use FA if the spectra can be pre-processed by deconvolution with a suitable broadening function.

In Fig. 1 we show the electron energy spectra, $N(E)$, for Ar and Li ions on aluminum at various imping energies. The curves are normalized to equal areas to emphasize changes in the energy spectra; here we do not correct the spectra by energy-dependent transmission of the electron analyzer ($\propto E$) to ease visualization of the high electron energy structure. The results depicted in Fig. 1 show interesting features, some known

Fig. 1. Electron energy spectra induced by 0.85–5 keV Ar$^+$ and 1.5–5 keV Li$^+$ impact on clean Al surfaces. The spectra are normalized to equal areas.

and some new. We begin with the Ar case. In Fig. 1a we can observe the main contributions to secondary electron emission, i.e. the peak at low energy coming mainly from Ar$^+$ Auger neutralization but also including cascade electrons from this Auger process and from kinetic emission, and the high energy electrons coming from the Al-2p Auger transitions: LVV (broad structure) and LMM (peaks) from the initial states Al^0 ($2p^53s^2$-$3p^2$) and Al$^+$ ($2p^53s^23p$) decaying into Al^{2+} ($2p^63s$) and Al^{2+} ($2p^63p$) [9]. The evolution of the normalized curves with projectile energy shows the increasing importance of the Al-2p Auger contribution. The contribution of plasmon de-excitation, with a high-energy edge around 11 eV (plasmon energy minus surface work function), appears mostly shadowed by the Auger neutralization mechanism. Another interesting aspect is the existence of a crossing point in the normalized spectra [10], which is evidence that there are only two spectral components that evolve independently [11]. Although the application of FA by no means needs this condition, since its power is just based on its ability of determining the number of independent components, this crossing point gives independent support to the method. Both physically meaningful components, also detected through Factor Analysis, hereinafter named as factors 1 and 2, represent at least two different mechanisms of secondary electrons production. The qualifier ''at least'' represents the fact that FA can detect different mechanism as long as they show distinct dependences, i.e. two different mechanisms showing the same energy dependence will appear as a unique factor in our data treatment.

In Fig. 1b we depict normalized electron energy spectra corresponding to Li ions impinging on the Al surface. As expected, the energy spectra are quite different from those excited by Ar. We note the absence of the broad structure due to Auger neutralization, and the presence of the peak with a high-energy cutoff corresponding to plasmon de-excitation. Similar to the Ar-impact case, there is a prominent structure corresponding to Al-2p Auger transitions. The presence of electrons coming from the de-excitation of backscattered Li^{+*} ($2s^2$) [3] is not observed because of the significant broadening caused by the high ion velocity [3]

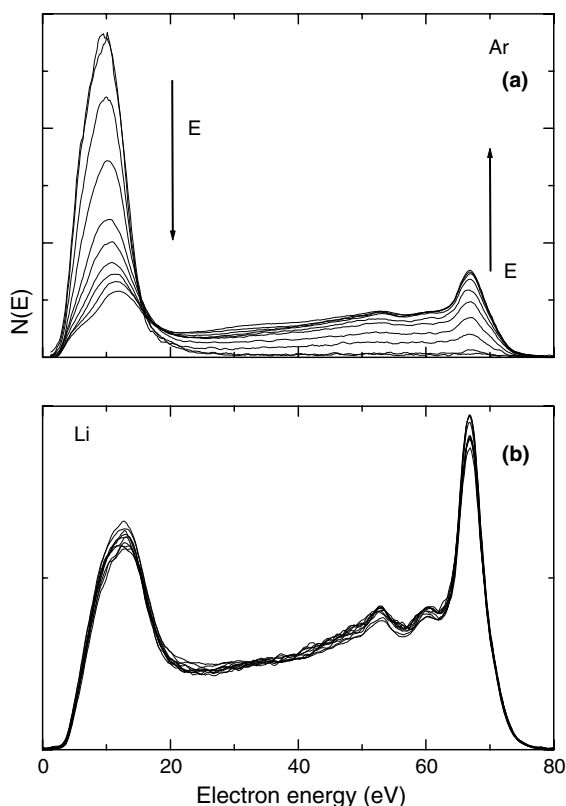and the wide range of observation angles in the cylindrical mirror analyzer. Such broadened structure contributes to the continuum below the two lower energy Ar-LMM Auger peaks. The most striking observation is that the shape of the energy spectra does not depend on energy. As mentioned above, such behavior should give only one factor within the FA procedure.

We now show a summary of the FA results. Fig. 2a has the shape of the factors (independent spectral components) obtained using FA for Ar^+ on Al. Fig. 2b shows the corresponding weights
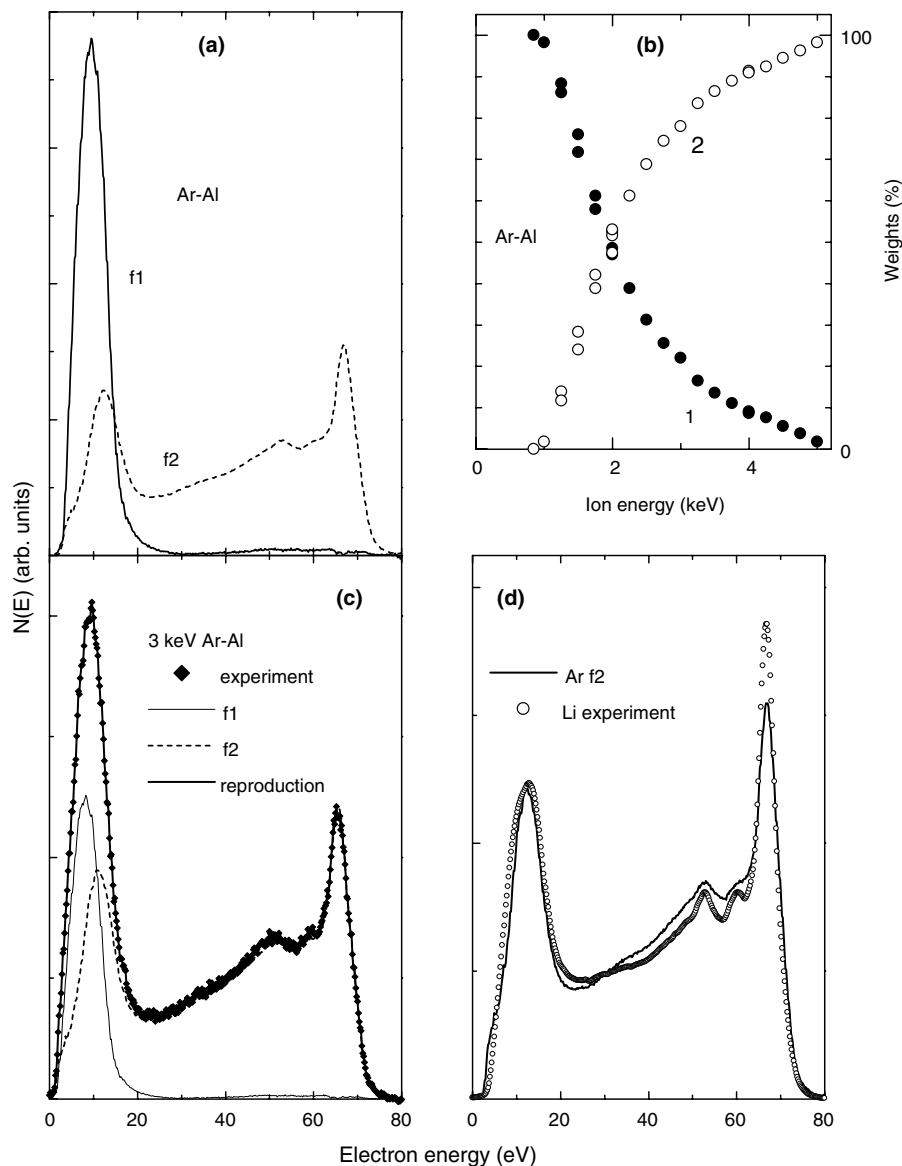

Fig. 2. (a) Factors 1 and 2 obtained by means of Factor Analysis of electron emission spectra induced by Ar^+ impact. (b) Weight of each factor vs. projectile energy. (c) Comparison between the experimental spectra, contribution of factors 1 and 2 and the spectra reconstructed from the factors for 3 keV Ar. (d) Comparison of factor 2 for Ar–Al and the averaged Li–Al experimental spectra.

vs. projectile energy. In Fig. 2c the experimental spectrum for 3 keV Ar$^+$ is depicted, together with the contribution of each factor in Fig. 2a, with the weights of Fig. 2b, and with the linear combination that fits the experimental result. The excellent fit demonstrates the ability of FA in decomposing experimental spectra. Finally, in Fig. 2d we compare factor 2 for Ar with the only factor obtained for Li.

In the following analysis we should keep in mind the key aspect of the FA method, which is that the electron spectra for all projectile energies can be reconstructed by a linear combination of the factors. The physically meaningful fact behind this point is that, within the sensitivity of FA, all the excitation mechanisms included in one factor have the same dependence with projectile energy; otherwise they would appear as independent factors. For Ar, we can visually identify two different parts in the factor 2 spectrum. The peak at low energies corresponds to the cascade of secondary electrons produced and to the plasmon decay electrons, produced by kinetic processes. At high energies, the Al-2p Auger transitions are clearly separated. We stress that, in this analysis, the plasmon decay contribution and the low energy electron cascade appear in the same factor as the Al-2p electrons, meaning that plasmons are exclusively generated by fast (mainly Al-2p Auger) electrons. This result is accomplished only by means of FA; the plasmon induced electron emission signature is by no means evident in the experimental spectra.

Our results for Li on Al show that Al-2p Auger electrons, plasmon decay electrons and cascade electrons have the same energy dependence. The simplest explanation is that they originate from the same primary mechanism, i.e. the excitation of Al-2p vacancies produces Auger electrons that in turn excite plasmons and the low energy electron cascade. Additionally, the similarity between the spectra generated by Li$^+$ and factor 2 in the Ar spectra is quite startling. We note here that one of them (Ar) was obtained from a data analysis, while the other (Li), since it corresponds to only one component in FA, is just an average of all the experimentally obtained spectra. Thus, our results show not only that the cascade plus
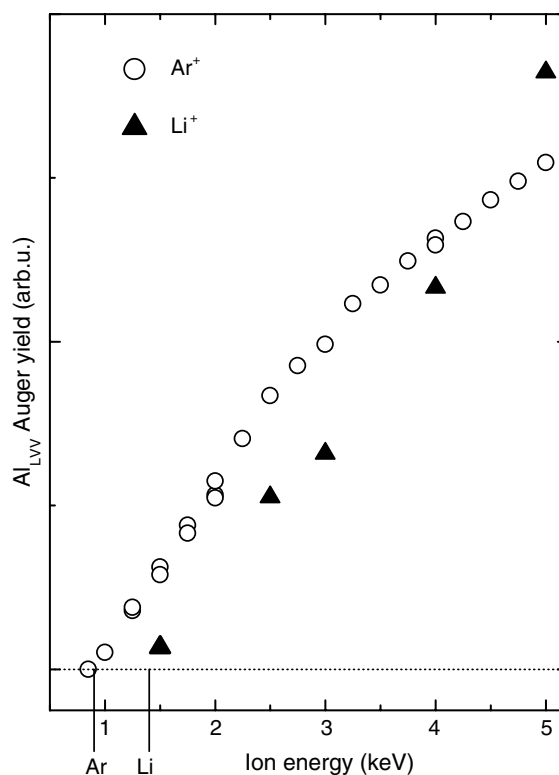

Fig. 3. Evolution of Al LVV Auger yield for Ar$^+$ (○), and Li (▲). The expected thresholds (0.9 keV for Ar and 1.4 keV for Li projectiles) are depicted as vertical lines on the energy axis.

plasmon induced features and Al-2p excitations are coupled, but also that the Al-2p excitation mechanism is probably the same for both incident ions. This idea is confirmed in Fig. 3, where we depict the Al-2p Auger yield for both cases. It has been established that Al-2p excitation in collisions of Ar ions with Al surfaces is due to symmetric Al–Al collisions in the atomic collision cascade started by the Ar projectiles [9]. This process has an Ar energy threshold of 0.9 keV [9], from which we calculate a threshold of 1.4 keV for Li ions. As shown in Fig. 3, these values are in good agreement with experiment, supporting the view that for Li projectiles, Al-2p electrons are also excited in Al–Al collisions.

In summary, through the novel application of the Factor Analysis method to electron emission spectra we are able to identify different mechanisms for electron excitation under ion bombardment.

Based on the electron emission distributions and incoming ion energy dependence, we separate the contribution of Auger neutralization from both plasmon de-excitation and cascade electrons due to kinetic excitation. We conclude that plasmons are produced by fast electrons and that in both cases, Ar and Li, Al-L Auger electrons (fast electrons) are produced through the same mechanism, symmetric Al–Al collision in the atomic collision cascade in the solid.

Acknowledgement

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