Broadening effects in Auger neutralization of 130–430 eV Ar⁺ ions at Al surfaces

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Abstract

We present a model for electron emission from Al surfaces by Auger neutralization of 130–430 eV Ar⁺ ions, that includes the singular response of the metal conduction band to the abrupt change of the surface potential caused by electron capture by the incident ion. This effect, previously identified in X-ray studies, produces a broadening that plays a significant role in reproducing the higher energy part of the experimental electron kinetic energy distributions.

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1. Introduction

Auger neutralization (AN) of slow ions colliding with metal surfaces is a powerful tool to obtain information on the electronic structure of the surface and on the evolution of ionic levels in the ion–surface interaction. The foundations of both experimental and theoretical treatments of Auger processes were established in the 1950s by Hagstrum [1]. Since then, many works of increasing sophistication have explored the characteristics of the kinetic energy distributions of the electrons collected during the collision and the charge state of the particles reflected from the solid [2–7].

In particular, the study of the experimentally observed broadenings of the kinetic energy distributions of ejected electrons was used to explain the basic physical effects taking part in AN [1]. It was early recognized that the dominant broadening component has a nearly Lorentzian structure,
which gives rise to a common intersection point (“magic” energy) for spectra acquired at different ion kinetic energies [3]. The Lorentzian broadening results from: (i) the asymptotic behavior of the matrix elements of the AN potential, producing a width scaling linearly with $v_\perp$, the perpendicular component of the projectile velocity to the surface; (ii) the average lifetime of the final state of the metal conduction band, involving two holes below the Fermi energy. Other sources of broadening were identified in: (iii) the lifetime of the initial state arising via the ion survival probability; (iv) the effect of variation of the energy level of the projectile near the surface of the target; (v) the shift of the Fermi energy. Other sources of broadening near the Fermi energy. In X-ray absorption, a \textit{transverse} photon couple to the electron density operator, whereas longitudinal photons couple to the electron current density operator, whereas longitudinal photons couple to the electron density operator via $\mathcal{H}_1 = 1/2 \int d^3r \Psi^\dagger(r_1) \varphi(r_1)\Psi(r_1)$. A convenient expansion for $\Psi$ is

$$\Psi(r) = \sum_k \langle r | k \rangle c_k + \langle r | a(t) \rangle c_a(t),$$

where: $\{ \langle r | k \rangle \}$ is the orthonormal set of the wavefunctions of the conduction band, of spectrum $\{ \varepsilon_k \}$, Fermi energy $\varepsilon_F$ and width $\xi$, Fermi energy $\varepsilon_F$ and width $\xi$, and $\langle r | a(t) \rangle$ is the ground state of the ion, corresponding to the ionization energy $\varepsilon_a(t)$. Explicit time-dependence is a consequence of the classical motion of the projectile that follows a straight-line trajectory of incident velocity $v$, perpendicular component $Z(t) = v_\perp |t| + Z_0$ and turning point $Z_0$, relative to the surface. Atomic and metal states are \textit{orthonormalized} as the ion approaches the vicinity of the surface [4], so that electron annihilations operators $\{ c_k, c_a(t) \}$ satisfy the ordinary algebraic rules of fermion operators.

The representation of $\mathcal{H}_1$ into the orthonormalized set yields two types of interaction: $\mathcal{H}_{\text{AU}}$, denoting the usual Auger potential [1,3,5] of matrix elements $V_{kk'}^{\text{AU}}(t) = \langle k|\langle a(t)|v_\text{sc}(r_{12})|k'\rangle|k'\rangle$ and $\mathcal{H}_{\text{E}}(t) = \sum_{k,k'} V_{kk'}^{\text{E}}(t) c_k^\dagger c_k^\dagger \langle a(t)|v_\text{sc}(r_{12})|a(t)\rangle$, that describes the abrupt change of charge due to neutralization of the incident ion and injection of a hole. It should be noted that $\mathcal{H}_1$ includes also the two body potential between metal electrons, that for certain projectile–target combinations may give rise to plasmon assisted neutralization [5,7].
However, we shall consider applications in which these effects have not been experimentally observed.

Eq. (2) has the same structure of the MND potential in the X-ray problem, where the core-hole potential operates as a scattering perturbation upon conduction electrons after the core state has been switched on. The Fock space is, therefore, partitioned into two subspaces: on the one hand, many electron states with the ion state empty, to all possible excitations of the excited state, of energy $e_k$, and two band holes. We can use the Fermi golden rule approximation, treating $\mathcal{H}_{\text{AU}}$ as a small perturbation, to write

$$N_1(e_k, v) \propto \rho_k \int d^2 \Omega_k \sum_{k', k''} \int_{-\infty}^{\infty} dt |V_{kk'}(t)|^2 \times F_{\alpha}(t, v, \pm) \exp \left(-\frac{\Delta_0}{2} \left| \sum_{k' k''} \right| \cdot \left| \sum_{k' k''} \right| \right) \times \exp \left(i \int_0^t dt \left[ e_k + \varepsilon_\alpha(\tau) - e_\alpha - q \cdot v \right] \right),$$

where $\rho_k$ is the density of states available to excited electrons, $q = k - k' - k''$ is the momentum exchanged in a single excitation process and $v_\parallel$ labels the component of the ion velocity parallel to the surface. Indeed, Eq. (3) comes from the Fermi golden rule with the correction of three ingredients: the lifetime of the initial and final states, the effect of the electron–phonon interaction and the change in the final state of the metal due to the sudden switching of the edge potential (2), caused by ion neutralization. $P_{\alpha}(t, v, \pm) = \exp \left(-\int_{-\infty}^{\infty} dt \right) \times [w_\alpha(\tau) + 2\Delta_0(\tau)]$ is the probability that the ion ground-state survives neutralization, due to both Auger and resonant processes. It includes the AN transition rate $w_\alpha$ [1–4] and the virtual width of the atomic state $\Delta_0$ [10] due to hopping processes; $\Gamma_0$, the lifetime of the band holes created by AN and $\sigma_{\text{PH}}$, the (Gaussian) broadening due to the electron–phonon interaction [8] at room temperature, describe velocity-independent effects that are outside the theory. Finally, $F_\alpha$ accounts for the nonorthogonality between the initial and final states of AN are not orthogonal the initial state.

The key quantity in our study is the distribution $N_1(e_k, v)$ of electrons excited above the Fermi level by the incident ion. $N_1$ is proportional to the differential cross-section for a transition from the unperturbed ground state $|\tilde{i}\rangle$ of the conduction band, with the ion state empty, to all possible excited states $|\tilde{f}\rangle$, with the ion state occupied, that involve the excited electron, of energy $e_k > e_F$ and two band holes. We can use the Fermi golden rule with the correction of three ingredients: the lifetime of the initial and final states, the effect of the electron–phonon interaction and the change in the final state of the metal due to the sudden switching of the edge potential (2), caused by ion neutralization. $P_{\alpha}(t, v, \pm) = \exp \left(-\int_{-\infty}^{\infty} dt \right) \times [w_\alpha(\tau) + 2\Delta_0(\tau)]$ is the probability that the ion ground-state survives neutralization, due to both Auger and resonant processes. It includes the AN transition rate $w_\alpha$ [1–4] and the virtual width of the atomic state $\Delta_0$ [10] due to hopping processes; $\Gamma_0$, the lifetime of the band holes created by AN and $\sigma_{\text{PH}}$, the (Gaussian) broadening due to the electron–phonon interaction [8] at room temperature, describe velocity-independent effects that are outside the theory. Finally, $F_\alpha$ accounts for the nonorthogonality between the initial and final states of AN are not orthogonal the initial state.

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the Fermi edge singularity. The broadening due to $u_{kk}^{\nu\nu}$ comes from the asymptotic behavior of the matrix elements of the AN potential. Using the approximate time dependence $V_{kk}(t) = V_{kk}^{(0)} \exp(-\lambda_{a}v_{\perp}|t|/2)$, $u_{kk}^{\nu\nu}$ becomes a Lorentzian function of constant width $\lambda_{a}v_{\perp}$. Neglecting the effect of the parallel velocity, the model simplifies to the well-known Hagstrum convolution model [1]. This approach introduces a “universal” function of the ion perpendicular velocity and the atomic level – convolution of $B(e, v_{\perp})$ with a Lorentzian of width $\lambda_{a}v_{\perp}$ – taking into account the broadening behavior of the electron spectra with the ion motion.

3. Experiments and applications

We measured the kinetic energy distributions of electrons ejected from polycrystalline Al surfaces, during the impact of 130–430 eV Ar$^+$ ions. Ar$^+$ ions were produced in an electron bombardment source operated at low electron energies (30 eV) to prevent significant contamination of the ion beam with doubly charged ions. The surface of the samples were normal to the axis of the spectrometer and at 12° with respect to the ion beam direction. The spectrometer was operated at a constant pass-energy of 50 eV (and, therefore, an approximately constant transmission over the measured electron energy range) and with a resolution of 0.2 eV. The high purity polycrystalline Al surfaces were sputter cleaned by 4 keV Ar$^+$ ions at 12° glancing incidence. The spectra were acquired with the sample biased at −2.5 V to separate the contribution of electrons emitted directly from the sample (which are accordingly shifted to higher energies) from a spurious peak of low energy electrons, mainly arising from the grounded entrance grid of the analyzer.

As shown in Fig. 1(a), the low energy peak structure tails exponentially and can be easily subtracted. After such subtraction, the spectrum is shifted backward by the bias voltage. The adequacy of this procedure can be seen by comparison with the spectrum acquired without the bias voltage, shown in Fig. 1(b), normalized to the same height. The corrected energy distributions of emitted electrons are displayed in Fig. 1(c) and show characteristic features of the AN process [1,3,5]: constant areas, i.e. total electron emission yields and a magic energy at 5.3 eV.

Fig. 1. (a) Kinetic energy distribution of electrons ejected from Al by 230 eV Ar$^+$-ions, with the sample biased at −2.5 V. (b) Corrected distribution, without the spurious peak of low energy electrons and spectrum acquired without the bias voltage. The spectra are normalized to the same height for comparison. (c) Corrected energy distributions of electrons ejected from Al by 130–430 eV Ar$^+$-ions, obtained as in Fig. 1(a) and (b).
The conduction band of Aluminum is specified by the parameters \( \xi = 15.95 \text{ eV} \) and \( \varepsilon_F = -\phi = -4.25 \text{ eV} \), in the Jellium approximation, while the ionization potential of Argon, at an infinite distance from the target is \( \varepsilon_0^\infty = -15.76 \text{ eV} \). We use the eigenfunctions of the Jennings potential as the starting basis set for the metal conduction band and for continuous sates above the vacuum level [11]. Resonant transfer processes to the excited states of Argon can be neglected although, far from the surface, the energies of these levels are close to the Fermi energy of Aluminum. In fact, the interaction with the metal shifts ion energies positively by \( \sim 1–2 \text{ eV} \). Thus, the most efficient neutralization mechanism of ejection involves only the ground state of the projectile, calculated by the pseudopotential of [12].

We approximate the electron–electron potential to the Thomas–Fermi expression \( v_{PF}(r_{12}) = \exp \times (-\mu r_{12}/r_{12}) \), where \( \mu \) is the inverse screening length due to other metal electrons. Both the unscreened Coulomb potential \( (\mu = 0) \) and more advanced dielectric screening models have been used for \( v_{sc} [3] \). The matrix elements \( V^{\alpha\beta}_{kk}(r_{12}) \) and \( V^{\alpha\beta}_{k0}(r_{12}) \) are worked out by Fourier transforming in the coordinates parallel to the surface [3] and numerically integrating over the coordinates perpendicular to the surface. Finally, the internal distribution \( N_{10} \) is calculated using Monte-Carlo techniques for multiple wave-vector integrals in Eq. (5).

As a first check, we test the basic theory of AN, corresponding to the replacement \( F_\ell(t,v_{\perp}) \rightarrow 1 \) in Eq. (6). The resulting external distributions \( N(E,v) \) depend on four free parameters, i.e. \( Z_0, \mu, \Gamma_0 \) and \( \sigma_{PH} \). It should be pointed out that no fitting procedure is required for their estimation. In fact, \( Z_0 \) is fixed by the condition that the pure spectrum coincides with the experimental electron energy distributions at the magic energy. Its value depends on the model used to calculate the atomic level shift \( \varepsilon_a(t) - \varepsilon_a^\infty \) at the time \( t \). With the approximations introduced in Section 1, \( \varepsilon_a(t) - \varepsilon_a^\infty \) results from the expectation value, in the state \( |\alpha(t)\rangle \), of the surface potential [11] and of the image potential of the scattering ion [12,13]. This calculation allowed us to estimate \( Z_0 \sim 4 \text{ Å} \) which corresponds to an energy shift of \( \sim 1.45 \text{ eV} \), at \( t = 0 \). More sophisticated calculations, including the chemical interaction between the ion and the metal at short ion-metal distances [14], may produce larger values for \( Z_0, \mu \) has a critical influence on the internal distribution \( N_{10} \) at excitation energies \( \varepsilon_k \) close to \( \varepsilon_F \). On the other hand, the line-shapes of both the internal and external distributions, at emission energies above \( \sim 2 \text{ eV} \), are unaffected by any choice of \( \mu \) in the range \( 0.05k_F \leq \mu \leq 1.00k_F \), \( k_F \) denoting the Fermi wave-vector. Finally, Previous studies have attested that \( \Gamma_0 \) is of the order of \( \sim 0.01 \text{ eV} [1] \) and \( \sigma_{PH} \sim 0.1 \text{ eV} [8] \).

Fig. 2 shows the theoretical spectra – for \( \mu = 0.1k_F \) and \( \Gamma_0 = 0.05 \text{ eV} \) – broadened by the experimental energy resolution, in which each internal function \( \mu_{\alpha\alpha}(0) \) has been obtained numerically from the Fourier transform of \( |V^{\alpha\beta}_{k0}(t)|^2 \). For completeness we also report the solution for a constant width \( \lambda = 1.83 \text{ a.u., extrapolated from the } \) asymptotic behavior of the numerical matrix elements \( V^{\alpha\beta}_{k0} \). We observe that the approximated distribution offers a qualitative good agreement with data since, in this context, the ion velocity is always small compared to the target Fermi velo-

![Fig. 2. The kinetic energy distribution of electrons ejected from Al by 130 eV Ar+-ions is compared with theoretical distributions calculated from the basic theory of AN (\( F_\ell(t,v_{\perp}) \rightarrow 1 \) in Eq. (6)) and from the approach of this paper (Eqs. (3)–(6)).](image-url)
ity. Consequently, the effective occupation of the target states in the rest frame of the projectile is very well described by the Fermi–Dirac distribution and shifted Fermi surface effects are small.

Fig. 2(b) shows the same distributions of Fig. 2(a), in the logarithmic scale. It is observed that theoretical calculations are in excellent agreement with the main part of experimental distributions for electron kinetic energies less than ~6 eV. However, the exponential behavior of spectra, at emission energies above the magic energy, is overestimated.

The MND theory [9,8] predicts an asymmetric line-shape for photoemitted electrons of the form \( (E - \varepsilon_0)^{\alpha - 1} \exp(-E - \varepsilon_b)/e_0 \), in which \( \alpha \) is a critical exponent depending on the phase-shifts of the screened core-hole potential, \( \varepsilon_b \) the core-state binding energy and \( e_0 \) a cut-off parameter. Such a broadening function seems to be the right candidate to cope with the observed high energy behavior of the spectra. We have modeled the correlation function \( F_\alpha(t,v_\parallel) \) with the same structure of the Fourier transform of the MND broadening function, i.e.
\[
F_\alpha(t,v_\parallel) \approx (1 + i\varepsilon_0(v_\parallel)t)^{-\alpha(v_\parallel)}.
\]

Adjustment of the parameters in Eq. (7) shows that \( \varepsilon_0 \) increases with increasing \( v_\parallel \), being of the order of the virtual width of the atomic state, i.e. \( \varepsilon_0 \approx 0.9-1.5 \) eV. \( \alpha \) is found also to increase in the range 0.12–0.16, the same order of the estimated value for the critical exponents of the measured 2s and 2p core lines of Al in X-ray photoelectron spectroscopy [8]. The modified electron distributions, calculated with the numerical internal functions \( u_{\alpha}^{\mu} \) – using \( \mu = 0.1k_F \) and \( \Gamma_0 = 0.01 \) eV – offer the correct exponential trend at higher energies, as reported in Figs. 2(b) and 3. It should be noted that \( \Gamma_0 \) was slightly overestimated in the previous analysis to compensate the absence the MND mechanism.

In summary, we extended the theory of Auger neutralization to include the effect of many-body shake-up of the valence electrons of the metal due to the abrupt change of the surface potential caused by electron capture by the incident ion outside the surface. The effect is manifested in the high-energy tail of the electron energy distribu-tions, where the theory accounts very well with the measurements. As a corollary, we expect the effect to be absent in materials with a band-gap. In such cases, although some form of shake-up will still occur, the effect on the electron energy distributions will be markedly different because of the absence of a Fermi-edge singularity.

References

