



Auger parameter and Wagner plot studies of small copper clusters



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ABSTRACT

We discuss application of the Auger parameter and Wagner plot concepts to the study of small copper clusters deposited on various supports such as C(graphite), SiO₂ and Al₂O₃. We demonstrate that the cluster size and the electronic properties of the support influence the shifts of both the binding energy of the Cu 2p_{3/2} transition and the kinetic energy of the Cu L₃M₄₅M₄₅; ¹G Auger transition. We find that the Cu L₃M₄₅M₄₅; ¹G-2p_{3/2} Auger parameter and Wagner plot allow one to single out and measure both initial- and final-state effects with a detail which is superior to that achieved in photoemission studies.

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1. Introduction

As is well known, the electron core-level binding energy, measured in photoemission experiments for a generic element, with a given oxidation state and a given chemical environment surrounding it, is a function of both initial-state and final-state effects [1]. The initial-state effect is a static contribution which depends on the ground-state orbital energies of the element before core ionization. The final-state effect depends on the degree with which the chemical environment polarizes in response to the switching-on of the core hole. Over the past three decades or so, many studies have aimed to single out the initial-state and final-state contributions that affect both the Cu 2p_{3/2} binding energy and/or the Cu L₃M₄₅M₄₅; ¹G Auger electron kinetic energy observed for small copper metal clusters and thin films deposited on various supports (diameter or thickness in the range of 5–25 Å). We here demonstrate that a heuristic approach, based on the use of the Auger parameter (AP) and Wagner plot (WP), offers a viable means for exploring the electronic properties of copper metal clusters as a function of two parameters, that is, the number of copper atoms making up the unit cluster particle and the chemical nature of the support. We stress that AP and WP analyses afford straightforward witness to both initial-state and final-state effects of copper core-level binding energy values.

The outline of the present paper is as follows: firstly, we recall the definitions of AP and WP arising from the combination of Cu L₃M₄₅M₄₅; ¹G-2p_{3/2} data for bulk Cu metal, Cu metal clusters and thin films; next, we review the findings reported in past photoemission studies of copper metal clusters and thin films deposited on various

supports; then, we discuss how AP and WP data account for the electronic properties of Cu metal clusters and thin films deposited on C(graphite), SiO₂ and Al₂O₃; finally, we compare our results with those of past photoemission studies.

2. The Auger parameter and Wagner plot concepts

Ab initio Hartree–Fock based studies by Bagus and co-workers [2] aimed to determine initial-state and final-state effects in photoemission experiments.

It is worth stressing that the insight into the electronic properties of a given system achievable by such theoretical approaches could be improved via simpler, semi-empirical methods, that is, by reducing the experimental data to the format of a Wagner plot, which also includes the Auger parameter.

More details on the formulation of the AP and WP discussed below can be found in the papers listed in Ref. [3].

2.1. Initial- and final-state effects

The general expression of the binding energy referenced to the Fermi level for the creation of a core hole left behind photoemission of the electron orbital c_i may be expressed as

$$E_b(c_i)^F(\text{atom/solid}) = E_b(c_i)^V(\text{free atom}) + k^0 Q^0 - kQ - [E_M(Q^0 - Q) + \Phi_{\text{solid}}] - R \quad (1a)$$

where E_b(c)^V is the binding energy of the free atom referenced to the vacuum level, Q⁰ and Q are the valence charges (in units of number of electrons) for the free atom in the gas phase and in the atom in the

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solid sample under study, k^0Q^0 (free atom) and kQ (atom/solid) represent the contribution to the core-ionization energy of the valence electrons with the factors k^0 and k that depend on the inverse of the valence shell radius of the free atom and the atom in the solid, respectively, $E_M(Q^0 - Q)$ is the Madelung energy, and Φ_{solid} is the work function of the solid sample.

The initial-state effect may be expressed as

$$I^F = E_b(c_i)^V(\text{free atom}) + k^0Q^0 - kQ - [E_M(Q^0 - Q) + \Phi_{\text{solid}}]. \quad (1b)$$

The final-state effect is the relaxation energy R , which has two contributions:

$$R = R^a(Q^0 - Q) + R^{\text{ea}}(\text{extra-atomic}). \quad (1c)$$

$R^a(Q^0 - Q)$ represents the atomic relaxation energy due to the valence charge difference between the atom under study and the free atom, and R^{ea} is the contribution arising from relaxation of electrons of neighbor atoms (extra-atomic).

To a first approximation $R^a(Q^0 - Q) \approx - (Q^0 - Q)R_1$, where R_1 is the relaxation energy per valence electron. For a core ionization of bulk metals ($Q \approx Q^0$), one can safely assume $R^{\text{ea}} \approx R_1$, that is a charge transfer of one extra-atomic electron from the environment toward the core-ionized atom.

In view of all this, the binding energy for a core electron photo-emitted from an element in the metallic state becomes

$$E_b(c_i)^F(\text{atom/metal}) = E_b(c_i)^V(\text{free atom}) + k^0Q^0 - kQ - [E_M(Q^0 - Q) + \Phi_{\text{metal}}] - R. \quad (2)$$

The net charge relevant to a metallic atom may well differ from Q^0 , and a difference may also occur whether the metal atoms sit on the surface or are in the bulk. In pure metals and in metal alloys, a charging of atomic sites and the attendant Madelung-like term may influence the core-electron binding energy. Moreover, the term $(k^0Q^0 - kQ)$ could assume negative values due to compression of the valence charge of the metal atom in the solid state with respect to the free atom. This corresponds, as expected [4], to a reduction of the metal core-electron binding energy.

The binding energy for the free atom referenced to the Fermi level is obtained from Eq. (2), given that $Q^0 = Q$, $k^0 = k$ and $R = 0$, one gets

$$E_b(c_i)^F(\text{free atom}) = E_b(c_i)^V(\text{free atom}) - \Phi_{\text{metal}}. \quad (3a)$$

According to Eq.(1b) this quantity represents $I^F(\text{free atom})$, then the shift in the initial-state effect with respect to the free atom is given by

$$\Delta I^F = k^0Q^0 + \Phi_{\text{metal}} - kQ - [E_M(Q^0 - Q) + \Phi_{\text{solid}}]. \quad (3b)$$

2.2. Auger parameter

The Auger parameter, initially defined by C. D. Wagner [5], is given by the general equation

$$\alpha' = E_k(c_1c_2c_3) + E_b(c_0) \quad (4)$$

where c_1 and c_0 represent two electron core orbitals of a given atom, and c_2 and c_3 are two electron core-core, core-valence or valence-valence orbitals of the same atom. (For present purposes, we shall apply Eq. (4) to the case in which $c_0=c_1 = 2p_{3/2}(L_3)$ and $c_2 = c_3 = 3d(M_{45})$.)

The kinetic energy of the Auger core-core-core electron and the binding energy of a core electron of the atom under study are added together to obtain a quantity that does not depend on the reference

level (the vacuum or the Fermi level) and, in the case of insulating solids, on any charging phenomena.

The kinetic energy of the Auger transition, with respect to the Fermi level, may be written as

$$E_k^F(c_1c_2c_3) = E_b^F(c_1) - E_b^F(c_2) - E_b^F(c_3) - U(c_2c_3) \quad (5)$$

where $U(c_2c_3)$ is the effective repulsion energy between the c_2 and c_3 holes in the $^{2S+1}L_J$ final-state term. This quantity may be also written as

$$U(c_2c_3) = R(c_2) + R(c_3) - R(c_2c_3) + F(c_2c_3). \quad (6a)$$

The term $F(c_2c_3)$ represents the LSJ-dependent bare repulsion energy between the c_2 and c_3 electrons, an electron interaction that does not depend on the chemical state of the atom. Considering that the relaxation energies are dominated by classical Coulomb contributions and applying Eq. (1c), that is $R(c_2) = R(c_3) = R(c_0) = R$, we obtain $R(c_2c_3) = 4R$, or, according to the formulation by Sawatzky and co-workers [7]

$$U(c_2c_3) = F(c_2c_3) - 2R. \quad (6b)$$

It can be shown [3,5] that

$$\alpha' = \alpha'(\text{free atom}) + 2R. \quad (7a)$$

According to Eqs. (1a)–(1c) and (4)–(6a)–(6b), and considering that for the free atom $R = 0$, we get

$$\alpha'(\text{free atom}) = [E_b^F(c_1) - E_b^F(c_2)] + [E_b^F(c_0) - E_b^F(c_3)] + F(c_2c_3) \quad (7b)$$

where the quantities $K_{12} = [E_b^F(c_1) - E_b^F(c_2)]$, $K_{03} = [E_b^F(c_0) - E_b^F(c_3)]$ and $F(c_2c_3)$ can be considered, to a good approximation, to possess a characteristic value for a given atom, regardless of its chemical state, with their sum equal to the Auger parameter of the free atom. (Cases where such approximations are not valid, e.g. sulfur and phosphorus compounds, are discussed in Ref. [3].)

2.3. Wagner plot

The kinetic energy of the $c_1c_2c_3$; $^{2S+1}L_J$ Auger electron, the binding energy of the c_0 core electron, and the Auger parameter ($c_0, c_1c_2c_3$; $^{2S+1}L_J$) can be displayed in a diagram called the Wagner plot, which is of considerable analytical utility. The Auger kinetic energy and the electron binding energy are usually referenced to the Fermi level. Note that the abscissa of the plot, $E_b^F(c_0)$, is oriented in the negative direction. The position in the plot of different chemical states of a given atom is determined by initial-state and final-state effects.

The natural reference chemical state is, of course, the free atom state. The Auger and photoemission data for the free atom are referenced to the spectrometer Fermi level using the work function of the bulk metal, see Eq. (3a)–(3b).

The following equations describe the rationale behind the Wagner plot and show how it can be used to estimate initial- and final-state effects.

It is possible to demonstrate that [3]

$$E_k^F(c_1c_2c_3) = I' - 3E_b^F(c_0) \quad (8)$$

where the quantity I' , called the *initial state parameter*, is given by the equation

$$I' = \alpha'(\text{free atom}) + 2 \{ E_b^V(\text{free atom}) + k^0Q^0 - kQ - [E_M(Q^0 - Q) + \Phi_{\text{solid}}] \}. \quad (9a)$$

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