COMMENTS

Comment on the "Blocking" Model for Auger Emission Intensity Maps from Surface Structures

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Received: February 4, 1993; In Final Form: March 16, 1993

In a recent paper, Frank et al.[1] report several angular distribution maps of Auger electrons from the systems Pt{111}-$(\sqrt{3}\times\sqrt{3})R30$-I, Pt{111}-$(\sqrt{7}\times\sqrt{7})R19.1$-I, and Pt{111}-(3×3)-I. While the experimental data appear to be good, Frank et al. use these data to provide support for their "blocking" model,[2,3] explaining that the angular distributions of Auger electrons are due to surface atom "blocking" or "shadowing" effects. They neglect the quantum mechanical wave nature of electrons, treating them as classical balls and surface atoms as spherical blockers. Their main discussions and conclusions contradict the basic principles of quantum mechanical scattering theory and a great deal of research carried out over the past few decades in this field.[4] Several similar papers by these authors have been heavily criticized within the science community.[5-12] Our comments are motivated by the appearance of a further paper utilizing this much criticized "model".[1]

Direct experimental evidence has been put forward to demonstrate the inappropriateness of the blocking model. (1) Terminello and Barton[9] revealed considerable differences in the intensity maps between the photoemitted and the Auger emitted electrons with the same kinetic energy, for Cu{100} with 56-eV electron kinetic energy. While some intensity minima are found along interatomic directions in the Auger electron intensity map, intensity maxima appear along the same directions in the photoelectron map. They attributed these differences to initial state (source wave) effects in scattering and specifically ruled out blocking as a mechanism: both photoelectrons and Auger electrons of the same energy should be equally "blocked" by the same atoms! (2) We showed[7] that the blocking model is incorrect for the interpretation of experimental data supplied by Frank et al., for the system I/Ag/Pt{111}, at a (Ag) Auger kinetic energy of 355 eV. Both single scattering theory intensity maps and a direct holographic transform of their data independently demonstrated, in agreement with LEED intensity analysis, that I adatoms are in 3-fold hollow Ag sites. The blocking model, however, placed I adatoms in untenable atop positions.

Theoretically, several groups have demonstrated the importance of initial state effects in electron emission intensity maps at low energies.[10-12] Barton and Terminello[10] calculated intensity maps from Cu{100} at 55 eV for Cu 3p photoelectrons and for Cu ($M_{2,3}M_{4,5}M_{4,5}$) Auger electrons, using s and d waves for photoelectrons and f waves for Auger electrons as source waves. The results reproduced the experimental intensity maps, without involving blocking, at these low kinetic energies. Recently, Idzerda and Ramaker[11] simulated intensity maps for electron emission from Cu{100}, Pt{111}, and Ag/Pt{111}, and again strong similarities to experimental data were obtained with appropriate initial states. Greber et al.[12] obtained similar results.

The Auger intensity maps which originally led Frank et al. to their blocking model were obtained at low energies from Pt{111}.[2,3] To demonstrate the origin of minima in the intensity maps along internuclear axes for given initial state conditions at low energies, we have calculated angular-dependent intensity profiles for a simple model involving two Pt atoms, using a quantum mechanical electron scattering formalism,[13] at 65 eV kinetic energy. The exact Green's function is used; one atom emits Auger or photoelectrons, and the other, situated above the emitter, scatters the emitted electrons, with inclusion of a Debye–Waller factor. As shown in Figure 1, the electron intensity profiles (diffraction intensities) were computed for s-wave ($l = 0$), p-wave ($l = 1$), d-wave ($l = 2$), f-wave ($l = 3$), and g-wave ($l = 4$) initial states. If s, p, or d waves are used, there is a strong peak along the interatomic direction due to constructive interference: the forward scattering peak. However, if the initial states are f or g waves, there is a dip in the same direction, due to destructive interference. If initial state effects are properly accounted for, there is therefore no need to involve a blocking mechanism. It should be stressed that the initial state effect will be much less pronounced at higher energies, ensuring constructive interference in interatomic directions; forward scattering is the rule at high energies.[10]

The blocking model can be properly addressed as anisotropic electron attenuation, or inelastic scattering. The range of inelastic scattering mechanisms is documented in the literature,[14] the most important being plasmon excitation. Taking aluminum as an example, from earlier calculations[15,16] it is clear that inelastic scattering due to plasmon excitation is dominated by valence electrons and is very homogeneous. Even for transition or noble metals, where d electrons are localized, Pendry[17] has pointed out that the incident electrons will interact with localized d electrons even when they are outside the d-electron charge density; the optical potential is less anisotropic than the electron density causing it. Considering inelastic scattering from Cu, Ing[16] concluded that the anisotropy amounts to less than 10% variation over the unit cell. In support of this conclusion, we cite the agreement between experiment and theory in LEED and photoelectron diffraction, based on the assumption that the inelastic scattering is homogeneous.[17,18]

The essence of the position represented by Frank et al. in their most recent paper[1] is that, despite the mountain of evidence against the classical blocking model, they have found a case, I on Pt{111}, where it "works". There are no LEED intensity analyses of the various I structures, so that atomic positions and spacings in the surfaces are *not* known, despite the implication in their paper. However, there is an STM study, which is certainly suggestive (though far from conclusive, as appreciated by the authors[19]) of the unit mesh of $(\sqrt{7}\times\sqrt{7})R19.1$ structure containing two I adatoms with different metal surface plane to adatom plane spacings. On the basis of this model, they claim good agreement with their spherical blocking model. However, the analysis does not stand up to a detailed scrutiny: agreement between experiment and model calculation is actually very poor. In each of their analyses, Frank et al. draw attention to the structure close to horizon: in the simulations, this is between 75 and 90° polar angle. However, in the range 75–50° the simulations are uniformly structureless as a function of azimuthal angle, while the experimental data show considerable structure. Any agreement is clearly entirely fortuitous, which is hardly surprising: diffraction effects are bound to dominate the intensity maps, and these are necessarily excluded from the blocking model.

This model has no basis in quantum mechanics and no experimental validation. In particular, it is quite inappropriate as a tool for structure determination: at low electron kinetic energies a full quantum mechanical electron scattering calculation is required (Figure 1) to know whether or not scattering is enhanced along interatomic directions. At high kinetic energies (>300 eV) scattering will always be enhanced in this forward

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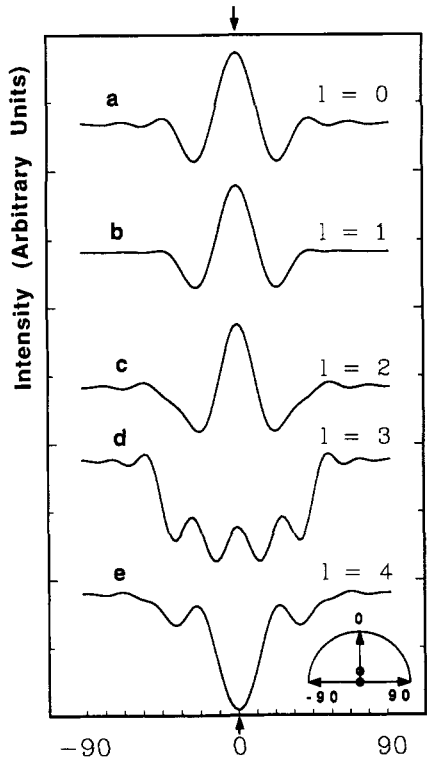

Figure 1. Angular-dependent intensity profiles of electron-emission diffraction from a two-atom model. The scattering geometry is shown in inset at the lower right-hand corner. The bottom atom emits electrons which are scattered by the atom above it. The curves a, b, c, d, and e are the diffraction intensities between s (l = 0), p (l = 1), d (l = 2), f (l = 3), and g (l = 4) source waves and scattered waves, respectively. The arrows mark the interatomic direction. Curves a to c illustrate forward scattering, while curve e reproduces an apparent blocking effect, due to destructive interference.

direction; as clearly shown in the I/Ag case,[7] the assumption of blocking gives an incorrect structural model. We do not believe that it justifies any further consideration.

References and Notes

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