

## Inverse photoemission from Ag(111) calculated by a multiple-scattering method

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Calculations of angle-resolved ultraviolet bremsstrahlung isochromats, using a multiple-scattering method, are presented for the first time for Ag(111). Good agreement is found with experimental data, both for surface- and bulk-derived spectral structures.

### INTRODUCTION

Angle-resolved inverse photoemission spectroscopy is currently being adopted as a tool for studies of unoccupied electron states in solids. To establish the ability of the method, experiments have been performed on well-defined systems with relatively well-known electronic structures, such as noble-metal surfaces. Among these the Ag(111) surface has been studied by several authors.<sup>1,2</sup>

Recently we presented isochromats from Ag(111) measured at 10.8 eV photon energy up to 21 eV above the Fermi level, for polar angles varying from 5° to 65° along  $\bar{\Gamma}-\bar{M}$  and  $\bar{\Gamma}-\bar{M}'$  azimuths (bulk  $\Gamma LU$  mirror plane).<sup>2</sup> The angle between the electron and photon beams was constant and equal to 90°, which restricted our experiments to off-normal incidence angles. For low polar angles the near-edge structures of our isochromats agreed well with those published by Reihl *et al.*,<sup>2</sup> but some differences occurred for polar angles greater than 20°. Most of our measurements covered previously unexplored phase-space regions. We found unusually intensive peaks in the energy range 10–20 eV above the Fermi level, which we could ascribe to direct transitions between bulk bands.<sup>3</sup> The energy positions of these strong peaks, as well as their dispersion agreed qualitatively with those theoretically predicted by a simple empty lattice model (or better by transitions between initial free electron states and final states obtained with relativistic augmented-plane-wave calculation).

In this communication we apply a multiple-scattering formalism to calculate isochromats from Ag(111) mainly at 35° electron incidence in the  $\bar{\Gamma}-\bar{M}$  and  $\bar{\Gamma}-\bar{M}'$  azimuths. The scheme, originally developed for calculations of angle-resolved photoelectron spectra,<sup>4</sup> is based on the close formal connection between photoelectron emission and inverse photoemission processes.<sup>5,6</sup> The formalism treats surface and bulk processes on the same footing and results in spectra with predicted peak positions as well as relative amplitudes. Some calculations of this type have been reported in literature.<sup>7,8</sup>

### THEORY

Our computational method is essentially that described extensively by Hopkinson *et al.*<sup>9</sup> The crystal is assumed to be composed of a stack of identical layers, each layer

containing one atom per two-dimensional unit cell. The potential at the atom sites is spherically symmetric and between the spheres a constant potential is assumed (muffin-tin approximation). We have used for Ag the self-consistent, nonrelativistic potential of Moruzzi *et al.*<sup>10</sup> The fundamental ingredients are the atomic-scattering phase shifts, which are calculated from the given muffin-tin potential. The effects of the multiple scattering of the incident electron plane wave within a layer are represented by the reflection and transmission matrices for that layer. The scattered plane waves are used as incoming waves for the next layer. By this procedure the total wave fields at energy  $E$  (initial state) and  $E - h\nu$  (final state) can be obtained. The two states are coupled via a dipole operator describing the radiative decay.

The surface barrier was modeled as a modified image potential according to McRae and Kane.<sup>11</sup> At large distances ( $z > \xi$ , see Fig. 1) this potential has the pure image form

$$U(z) = -1/4z .$$

At intermediate distances ( $0 < z < \xi$ ) we have for simplicity chosen to use a linear form, smoothly joining at  $z = \xi$ ,

$$U(z) = z/4\xi^2 + U_0 .$$

The corresponding phase shift can be written as

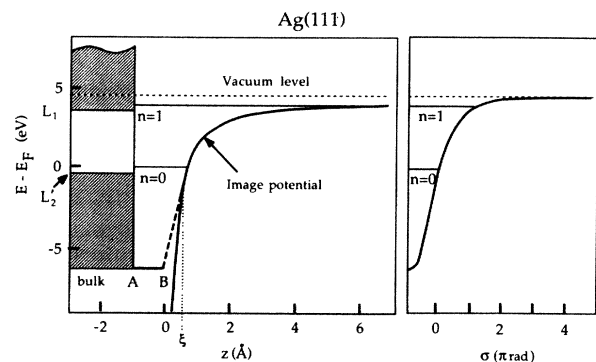


FIG. 1. Schematic drawing of the surface potential used in the present work. Also shown is the projected bulk band structure and the energy levels of a surface state ( $n=0$ ) and an image ( $n=1$ ) state.

$$\sigma(\varepsilon) = 8^{-1/2}(-\varepsilon)^{-1/2} + a_0 + a_1(-\varepsilon)^{1/2} + a_2(-\varepsilon), \quad |\varepsilon| \leq |\varepsilon_0|$$

$$\sigma(\varepsilon) = -1 + b_1(\varepsilon + U_0)^{1/2} + b_3(\varepsilon + U_0)^{3/2}, \quad |\varepsilon| \geq \varepsilon_0$$

$$\varepsilon_0 = -\frac{1}{4}(2 + U_0).$$

The energy  $\varepsilon(H)$  is referred to the vacuum level. McRae and Kane<sup>11</sup> have calculated the phase shifts at three energies  $\varepsilon$  for various sets of the potential parameters. The procedure is then, starting from a potential, to find the three phase shifts by interpolation. Requiring a smooth joint at  $\varepsilon_0$  determines the phase shift functions (five parameters) above.

In the actual calculations the inner potential at the surface was assumed the same as in the bulk. Thus the only variable parameter in the final computer calculations was the distance between the first layer of atoms and the image plane. This is chosen to reproduce some observed surface related features in the spectra, see further below. Although still primitive, this potential is superior to the step potential used in the published version of the program. Using the step potential one surface state may be reproduced but of course not the image states. For accurate quantitative results a more realistic, ultimately self-consistent potential should of course be used.

The effect of finite lifetimes of initial and final electrons was introduced via a negative, energy-dependent imaginary part  $V_i$  in the potential. In the present calculations we have used the following free-electron form:

$$V_i = -3.90(E - E_0)^{1/2}/\lambda,$$

where  $E_0$  is the inner potential and  $\lambda$  the electron mean free path. The energy dependence of  $\lambda$  was fitted to the "universal curve"<sup>12</sup> and found to be

$$\lambda (\text{\AA}) = \exp[5.59 - 1.08 \ln(E - E_F)].$$

All theoretical isochromats presented here have been additionally convoluted with a Gaussian to simulate experimental broadening.

Due to the fact that the calculation scheme was originally developed for photoemission, separate calculations were made for *s* and *p* polarizations of the emitted light. As these states are not distinguished in any experiment so far, the final polarization-dependent spectra were obtained as superpositions of the two components. The calculations provide absolute numbers for the photon intensity per incident electron, so no further weighting of the two components was made.

As input parameters in the calculations we used the lattice constant<sup>10</sup>  $a_0 = 4.12 \text{ \AA}$ , the Fermi energy<sup>10</sup>  $E_F = 6.54 \text{ eV}$ , the work function<sup>13</sup>  $e\phi = 4.7 \text{ eV}$ , and the self-consistent potential of Ag from Ref. 10. The plane-wave representations between the layers included 13 beams, the number of atomic layers was 32 in the high-energy and 128 in the low-energy state, and the spherical-wave expansions included components up to  $l = 4$ .

## RESULTS AND DISCUSSION

Among the experimental criteria employed to distinguish surface- from bulk-derived spectral features, the simplest one is to test their sensitivity to modified surface conditions (e.g., contamination or disorder). In the present calculation scheme we are able to make the distinction simply by observing spectral changes caused by modifications in the surface potential. With the model surface potential outlined in Fig. 1, there is one parameter which may be adjusted, namely the distance between the outermost atomic layer and the image plane (distance *A-B*). This adjustment is made here by comparison with photoemission spectra from the Ag(111) surface,<sup>14,15</sup> which show a crystal induced surface state ( $n = 0$  in Fig. 1) just below  $E_F$ . Figure 2 shows the effect of shifting the image plane from 1.15 to 0.95 Å outside the first atomic layer. As expected, the energy of the lower-lying bulk-derived peak ("B") remains unaffected by this change. The crystal induced surface state ("SS") is found to shift from a position just below the  $L'_2$  band edge into the  $L'_2$ - $L_1$  band gap. Its position becomes 0.25 eV below the Fermi level compared to 0.1–0.2 eV observed experimentally.<sup>14,15</sup> The energy of the lowest image state (IS) becomes 4.34 eV above the Fermi level while it is observed at 3.8–4.1 eV.<sup>13,16</sup> Within the model potential described above it was not possible to reproduce the two surface states with the same accuracy. Since our prime aim was to calculate the whole spectrum with sufficient accuracy to allow for spectral identification, we did not attempt to optimize the surface potential. Work concentrating on this problem has been published recently by other authors.<sup>17,18</sup>

The calculated *s*- and *p*-polarized isochromats from Ag(111) at 35° incidence angle in the  $\bar{\Gamma}-\bar{M}$  and  $\bar{\Gamma}-\bar{M}'$  azimuths are shown in Figs. 3 and 4. The photon and elec-

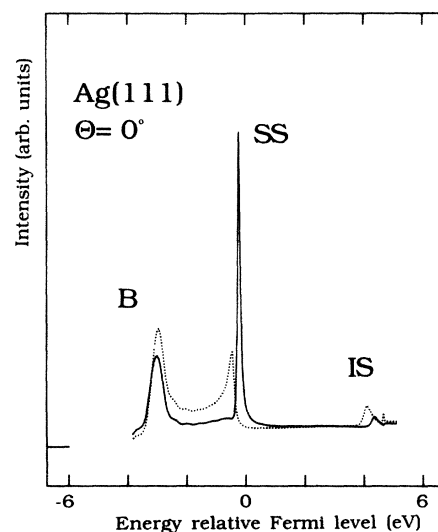


FIG. 2. Calculated photoemission and isochromat curves for the electron beam normal to the surface. The effect of translating the surface potential is illustrated: solid and dotted curves correspond to the image plane at 0.95 and 1.15 Å outside the outermost atomic layer, respectively.

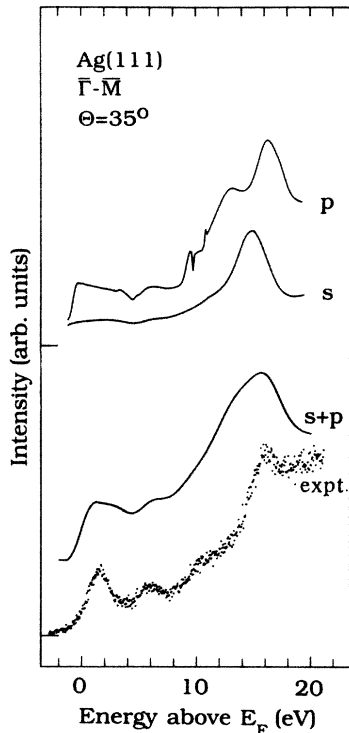


FIG. 3. Calculated (solid lines) and experimental (dotted) isochromats from Ag(111) for 35° incidence angle in the  $\bar{\Gamma}-\bar{M}'$  azimuth.

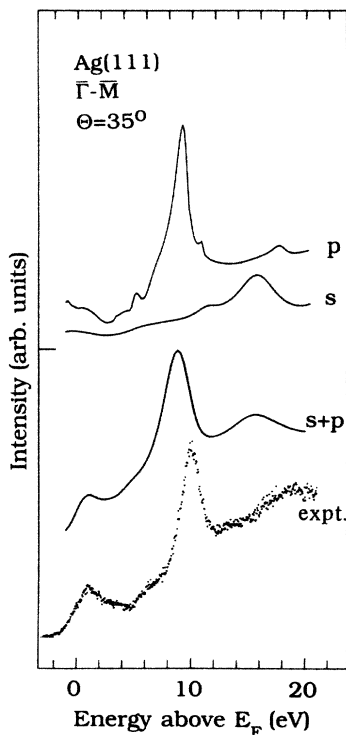


FIG. 4. Calculated (solid lines) and experimental (dotted) isochromats from Ag(111) for 35° incidence angle in the  $\bar{\Gamma}-\bar{M}$  azimuth.

tron beams were orthogonal as in our experiment. One striking result from these calculations is the great difference between the two states of polarization. As already pointed out, the experiment does not distinguish between these polarizations, but from the present results the advantage of such ability is obvious. The calculated isochromats for  $s$  polarization are similar at the two azimuths, showing only weak structures and an overall low intensity. For  $p$ -polarized light the spectra are very different in the two symmetry directions. For example, towards  $\bar{\Gamma}-\bar{M}$  one can see the pronounced peak appearing about 9 eV above the Fermi level, while in the  $\bar{\Gamma}-\bar{M}'$  azimuth this peak is completely absent.

In the already mentioned band-structure-based analysis<sup>3</sup> the most prominent structures were identified as bulk interband transitions. So, for example, the major peak near 10 eV in the  $\bar{\Gamma}-\bar{M}$  azimuth is due to a transition involving mainly  $\Delta\mathbf{G}=[022]$ . The intensity of this peak has a maximum  $\sim 45^\circ$  incidence angle, when the transition occurs near the  $\Sigma$  symmetry line in the fcc Brillouin zone. Likewise, in the  $\bar{\Gamma}-\bar{M}'$  azimuth the relatively strong peak near 16 eV is traced to a transition involving  $\Delta\mathbf{G}=[113]$ . At 35° incidence angle this transition is located near the  $L$  point. In the present calculations these structures were indeed found to be insensitive to variations of the surface potential, which confirms their bulk origin.

In Figs. 3 and 4 we also show the comparison between the total calculated spectra, obtained as direct superpositions of the  $s$ - and  $p$ -polarized components, and experimental isochromats.<sup>3</sup> The overall general agreement between experiment and theory is obvious. There are, however, some minor differences which deserve commenting. We note that the only prominent structure in the  $s$ -polarized spectra, i.e., the broad peak  $\sim 15$  eV above  $E_F$ , does not appear in any appreciable intensity in the experiment. This is particularly clear in the  $\bar{\Gamma}-\bar{M}$  azimuth, where the  $p$ -polarized spectrum is structureless in this energy range. This discrepancy can be caused at least partly by the complete negligence of light refraction and inner reflection at the metal-vacuum interface. Using the bulk index of refraction for Ag at 10 eV photon energy, we estimate that the transmitted  $s$ -polarized intensity should be reduced relative to the  $p$ -polarized intensity by  $\sim 25\%$ . However, since we are dealing with surface processes, direct application of Fresnel's equations may be questionable and we prefer not to make any such corrections at present. An interesting aspect is a possible contribution corresponding to the surface induced photoemission. So, for instance, a strong deviation between a theory based on Fresnel's equations and observed photoyield from Ag around 10 eV photon energy has been reported.<sup>19</sup>

Another observation is that some systematic differences occur between the experimental and calculated peak positions. These deviations are not unexpected. Firstly the potential used is nonrelativistic, which will produce somewhat too low energies.<sup>20</sup> Secondly one knows that dynamical exchange and correlation effects, not included here, will give rise to shift of about 5–10% of the energy relative to the Fermi level.<sup>21</sup> It is of course

feasible to introduce these corrections,<sup>22</sup> but it is clear that without these refinements the experimental results are well reproduced by the calculations.

### SUMMARY

The multiple-scattering method has been used for calculation of angle-resolved ultraviolet bremsstrahlung isochromats from Ag(111) in an energy range up to 20 eV above the Fermi level. A modified image potential was introduced as the surface barrier potential to reproduce

surface related states. Our results show that the calculation scheme is very well adapted for evaluation of inverse photoemission data.

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