Natural linewidth of the Ag(111) *L*-gap surface state as determined by photoemission spectroscopy

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(Received 15 December 1999; revised manuscript received 14 February 2000)

The Ag(111) surface state in the *L* gap has been measured at $T=30$ K by high-resolution photoemission spectroscopy ($\Delta E=3.7$ meV). The experimental linewidth (full width at half maximum) at normal emission is less than 10 meV, from which an internal lifetime width of the surface states of $\Gamma_{tot}=6.2\pm0.5$ meV is deduced. This value agrees with theoretical predictions but is smaller than the result obtained by a recent low-temperature scanning tunneling experiment, which gave a lifetime width equivalent to $\Gamma=9.8\pm1.2$ meV.

I. INTRODUCTION

The past decades have seen a considerable understanding of the electronic structure of solids and surfaces, where many of the interesting results have been obtained by photoemission spectroscopy. Only recently successful attempts to measure the dynamics of excited electron states have been performed. The knowledge and understanding of electron dynamics on surfaces is important to understand, e.g., chemical reactions on surfaces. Furthermore, a long-standing discussion about the line shape and lifetime width of the spectral function in many-body systems (e.g. the high-temperature superconductors) has stimulated lifetime investigations on simple model systems under well-defined experimental conditions. Improving and establishing the available experimental techniques is therefore of considerable importance.

There are basically two different methods to determine the lifetime of an excited state: one is by measuring directly the decay time τ (in this case by two-photon time-resolved photoemission spectroscopy),[1–3] the other one relies on a direct measurement of the spectral linewidth Γ of a quasiparticle excitation in the energy space, which is related to the inverse lifetime by $\Gamma=\hbar/\tau$. The theoretically predicted lifetime width Γ for quasiparticle excitations in simple metals lies typically in the range between 1–10 meV at low temperature (1 meV corresponds to a lifetime of $\tau\approx0.67\times10^{-12}$ sec), a regime that has recently become available to photoemission spectroscopy[4,5] (PES) and is accessible to time-dependent techniques[1–3] and scanning tunneling spectroscopy (STS).[6–8]

In a three-dimensional solid the spectral linewidth of a photoemission excitation is determined by the lifetime of the photohole state, in which one is interested in the present context, because it reflects the initial-state lifetime, but also by the electron lifetime of the final-state photoelectron, which very often dominates the experimentally observed linewidth and is hard to subtract.[9] If one works, however, with two-dimensional systems it can be shown that by kinematic considerations the electron linewidth drops out and one is able to measure the lifetime of the photohole directly.[10,11] One example for two-dimensional systems is surface states, and here the *L*-gap Shockley-type surface state on the (111) surface of noble metals has played a special role as model systems for the investigation of two-dimensional electron systems.[12] It is therefore tempting to try to measure the linewidth of such a surface state as accurately as possible and to compare it with theoretical calculations or the results of other measurements.

The *L*-gap surface state on Ag(111) is particularly interesting, because for this surface state an alternative and intrinsically very accurate method has been used to determine the natural lifetime width, namely, STS.[6,7] This landmark experiment has the advantage that in a first step one can carefully select an almost perfect, defect-free area ($\geqslant3000$ nm^2) of the surface at which subsequently the surface state and in particular its lifetime width is determined. This experiment resulted in an intrinsic full width at half maximum (FWHM) of $\Gamma=9.8\pm1.2$ meV, about half the value previously determined by PES ($\Gamma=19.9$ meV),[13] an experiment that is integrating over a relatively large surface area (typically $\gtrsim1$ mm^2) and contains contributions from surface imperfections over the whole investigated surface range.[14] The STS result was identified as the pure imaginary part Σ of the electron self-energy, corresponding to a lifetime of $\tau=66\pm8$ fs, and therefore gives the smallest experimental natural linewidth $\Gamma=2\Sigma$ for this system until now.

In addition the Ag(111) *L*-gap surface state is—because of its narrow linewidth and well defined dispersion—particularly suitable for the characterization of a high-performance photoelectron spectrometer with respect to energy and angular resolution. Much to our surprise, our spectra showed extremely narrow peaks, yielding a linewidth even smaller than that of the STS experiment, namely, 6.2 ± 0.5 meV. This value is very close to the theoretical value of 5 meV at $T=0$ K calculated by Berndt *et al.*[7] Contributions from thermally generated phonons at the chosen sample temperature of $T=30$ K increase this theoretical value only by approximately 0.5 meV.

The spectral linewidth of an electronic state in a metal is determined by three lifetime-related contributions, namely, the electron-electron interaction $\Gamma_{e\text{-}e}$, the electron-phonon $\Gamma_{e\text{-}ph}$, and the impurity scattering $\Gamma_{e\text{-}i}$, which can be summed up independently[15] to give the total internal linewidth

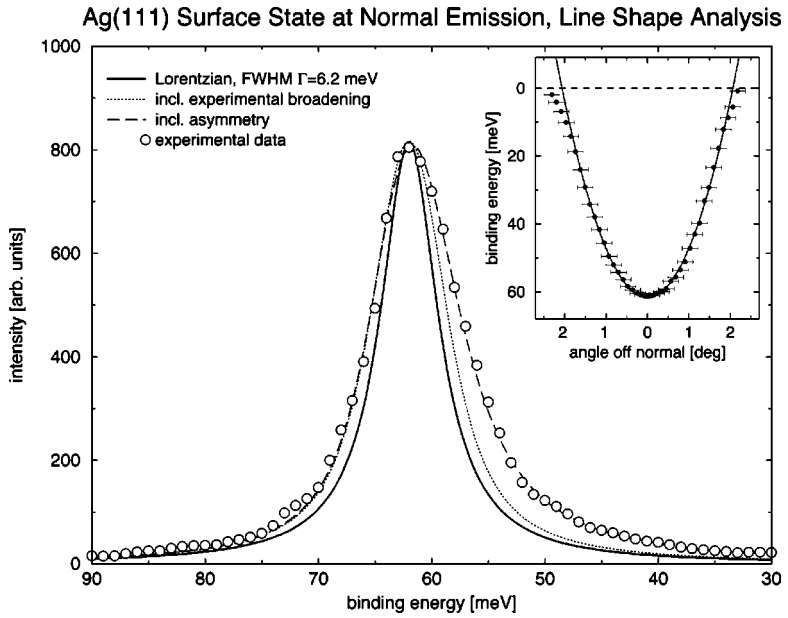

FIG. 1. Line-shape analysis of the Ag(111) surface state taken by photoemission spectroscopy (He I: $h\nu=21.23$ meV) in normal emission at $T=30$ K (open circles), the total experimental FWHM amounts to 9.5 ± 0.5 meV. The spectrum can be decomposed in a Lorentzian (FWHM $\Gamma=6.2$ meV, solid line) convoluted with the energy resolution function (Gaussian with FWHM $\Delta E=3.7$ meV) and an asymmetry factor of 18%, to describe the low-binding-energy tail (dashed). The dotted curve fits to the left part of the spectrum and includes only lifetime and instrumental broadening. The inlet shows the dispersion of the peak maximum (black dots). For small binding energies ($\lesssim 10$ meV) the Fermi distribution shifts the apparent peak maximum away from the Fermi energy. A fit with a parabolic dispersion (solid line, fit only for maxima at $\gtrsim 10$ meV) yields a value of $m^*/m_e=0.40\pm0.01$. The effective angular resolution $\Delta\theta_{\text{eff}}$ is indicated as horizontal error bars.

$$\Gamma=\Gamma_{e\text{-}e}+\Gamma_{e\text{-}ph}+\Gamma_{e\text{-}i}. \tag{1}$$

The first two terms in Eq. (1) are energy dependent and can be expressed by

$$\Gamma_{e\text{-}e}=2\beta[(\pi k_{\mathrm{B}}T)^2+\omega^2] \tag{2}$$

for the three-dimensional electron-electron scattering and

$$\Gamma_{e\text{-}ph}(\omega,T)=\int_0^\infty d\omega'\,\alpha^2F(\omega')[2n(\omega')+f(\omega'+\omega)+f(\omega'-\omega)] \tag{3}$$

for the electron-phonon interaction. $\alpha^2F(\omega)$ is the Eliashberg coupling function, $n(\omega)$ and $f(\omega)$ are the Fermi-Dirac and Bose-Einstein functions.

In addition to these intrinsic contributions, the experimental photoemission spectra will be broadened by the finite energy resolution, which can be described by convoluting the natural Lorentzian given by Γ with a Gaussian with FWHM$=\Delta E$. Furthermore a non-perfect, particularly a stepped, surface causes an asymmetric peak broadening.[16]

II. EXPERIMENT

The experiments were performed with an photoelectron spectrometer equipped with a monochromatized VUV source (GAMMADATA) and a Scienta SES-200 photoelectron analyzer, used in the angular mode for the data presented here. The parallel detection allows us to measure an angular window of approximately 15° simultaneously. Already at a photon energy of $h\nu=21.23$ eV (He I) this angular window encloses the complete k space where the surface state lies below the Fermi energy E_F. The angular resolution of the analyzer in this mode is $\Delta\theta=0.2°$; the net energy resolution, consisting of broadenings from light source (He I) and analyzer, amounts to $\Delta E=3.7$ meV (determined from an polycrystalline Ag Fermi edge at $T=8$ K). The recorded sample area is approximately 1 mm^2, given by the finite light spot of the VUV source. The base pressure was 5×10^{-11} mbar. During the measurement with the VUV discharge lamp the pressure raised to 8×10^{-10} mbar He. The sample temperature could be cooled down to $T=8$ K, but the measurements presented here have been performed at $T=30$ K, which reduces the deterioration speed of the sample surface.[17] The Ag single crystal (thickness $d=2$ mm, diameter $\varnothing=10$ mm) was cleaned by the standard procedure, i.e., a number of cycles of mild argon-ion sputtering and annealing at $\approx 500\,°$C by reverse-side electron bombardement for several hours. The cycles have been repeated up to typically 10 times until the linewidth of the Ag(111) surface state at normal emission (Γ point) had converged to the experimental minimum value reported here. After this procedure the resulting spectra did not depend on the investigated position on the sample surface.

III. RESULTS

Ever since the Ag(111) L-gap surface state had been detected for the first time in PES (Ref. 18) there have been much interest on this spectral feature over the years.[12,19,20] The most recent photoemission data has been published by Paniago *et al.*,[13] showing a slightly asymmetric line with a total experimental linewidth of FWHM$=35$ meV at an en-

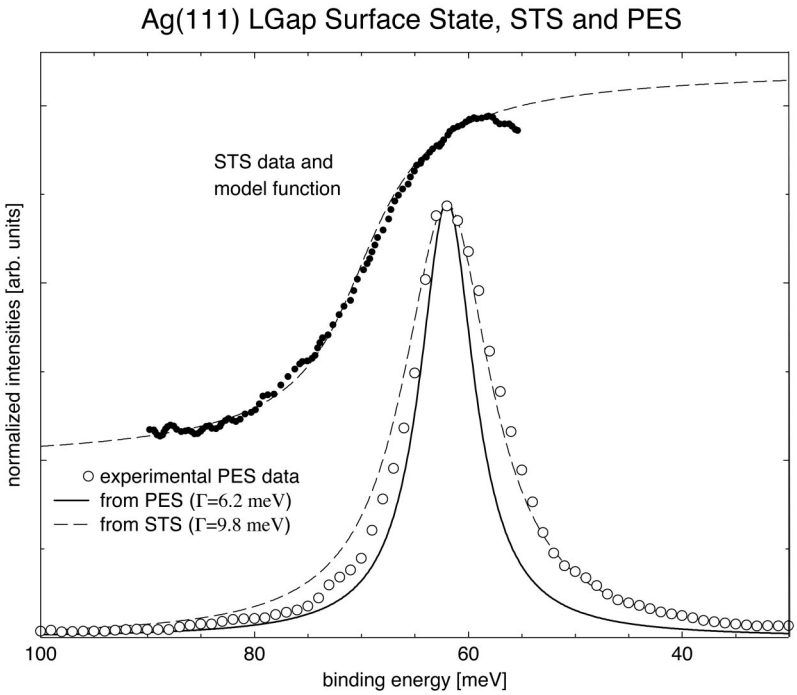

FIG. 2. Comparison of scanning tunneling spectroscopy (STS) at $T=5$ K (i.e., dI/dV vs sample voltage) and the photoemission data ($T=30$ K) of the Ag(111) surface state. The experimental STS data (black dots) are extended by the unbroadened model function describing a lifetime contribution of $\Gamma=9.8$ meV (dashed line). The corresponding Lorentzian (shifted by about 8 meV towards E_F) is shown below (dashed), compared with the experimental photoemission data (open circles) and its internal Lorentzian contribution (solid line).

ergy resolution of $\Delta E=21$ meV. Here the asymmetry is assigned to the finite angular resolution of $\Delta\theta=\pm 0.9°$. Because of this peak asymmetry only the high-binding-energy side, which is supposed to be free from this additional contribution, was used for the analysis and gave a lifetime width of about $\Gamma=20$ meV.

Figure 1 shows a typical Ag(111) surface state spectrum taken in normal emission at a sample temperature of $T=30$ K (open circles), without any background correction applied. To extract the intrinsic lifetime contribution we modeled this spectrum by a Lorentzian (FWHM Γ), an asymmetry factor to describe the low-binding-energy tail (compare Ref. 16), and a Gaussian instrumental broadening with a FWHM$=3.7$ meV. This yields a Lorentzian FWHM of $\Gamma=6.2\pm 0.5$ meV for the intrinsic lifetime width of the *L*-gap surface state on Ag(111) (full line).

The effective angular resolution might differ from the instrumental value of $\Delta\theta=0.2°$ because of a finite deviation of the crystal orientation over the investigated sample area. This value $\Delta\theta_{\mathrm{eff}}$ can be easily determined from the data by analyzing the spectra at angles with strong *k* dependence, i.e., in the branches of the parabolic surface state dispersion (see inset Fig. 1). The angular broadening at e.g., 1.7° off normal leads to a total linewidth of less than 18 meV at this angle, equivalent to a maximum effective angular resolution of $\Delta\theta=0.38°$, indicated as horizontal error bars in Fig. 1. At normal emission this angular resolution has no effect on line shape and linewidth. The photoemission spectra of several *in situ* prepared surfaces showed only very slight changes in the individual line shapes. The main difference was found in the asymmetry, which is most likely due to a stepped surface, whose quality can differ from preparation to preparation.[16] A detailed discussion of the analysis will be published elsewhere.[21]

We have also performed experiments at $T=8$ K; however, at this temperature the sample surfaces deteriorate rapidly, presumably due to hydrogen adsorption,[17] and—since the linewidth between $T=8$ K and 30 K differed only by about 1 meV—the final analysis was done with the data taken at 30 K given in Fig. 1. Note that this line has about the same width as that obtained from a Tamm surface state at Cu(100) by Purdie *et al.* at $T=10$ K,[17] from which an inherent natural linewidth of $\Gamma=7$ meV was deduced.

In Fig. 2 our photoemission results are compared to the STS results of Li *et al.*[6] The top curve gives their experimental data and the unbroadened model curve [i.e., $\arctan(\omega/\Sigma)$], which represents the internal linewidth of $\Gamma_{\mathrm{tot}}=2\Sigma=9.8\pm 1.2$ meV. The first derivative of this model curve is a Lorentzian with a FWHM$=\Gamma$ and can therefore directly be compared to the photoemission spectra. The lower trace of the figure shows our experimental photoemission data as open circles. To compare STS and PES data the STS derivative (dashed line) is shifted by about 8 meV to the energy position of the PES data $E_B=62.5$ meV, which—within experimental errors—is identical with the data published by Paniago *et al.*[13] This shift is approximately twice as large as the value anticipated from the temperature dependence reported in Ref. 13 at the temperature difference of 25 K here. In spite of the higher temperature of the PES data—resulting in an increased phonon broadening $\Gamma_{e\text{-}ph}$, a difference that is, however, small in comparison to the total linewidth—the internal Lorentzian contribution ($\Gamma^{\mathrm{PES}}=6.2$ meV, solid line) is definitely narrower than the STS result ($\Gamma^{\mathrm{STS}}=9.8$ meV, dashed line).

We have at this point no explanation for this apparent difference between the tunneling and photoemission techniques. However, although the STS results look like a cleaner experiment—the influence of temperature and modulation voltage can be subtracted easily, large defect-free sample areas can be chosen, whereas photoemission is integrating over $\gtrsim 1$ mm^2—the data presented here suggest that there are still broadening mechanisms in the published STS data that contribute to the lifetime value determined by this technique. However, unpublished results of the same group[22]

indicate that electronic noise in the power supply of the tunneling microscope has yielded an additional, unnoticed broadening effect. Their new STS measurements agree completely with the present PES result. In addition, this group has recalculated the lifetime width and finds now a value of $\Gamma = 7.5$ meV, slightly larger than the PES and new STS result.

IV. SUMMARY

In summary we have presented high-resolution photoemission measurements on the Ag(111) *L*-gap Shockley-type surface state, which give internal lifetime contributions to the full linewidth smaller than the narrowest published surface tunneling spectroscopy results. With our data the difference between theoretically calculated lifetime contributions and the photoemission results is no longer existent. Our experimental value of $\Gamma = 6.2 \pm 0.5$ meV is a upper limit for the natural linewidth of this surface state.

ACKNOWLEDGMENTS

We thank Thomas Finteis (Saarbrücken) and Professor R. Claessen (Augsburg) for their valuable help in setting up the experimental arrangement, and Professor A. Goldmann (Kassel) for a number of very extensive discussions on surface state measurements by photoemission spectroscopy. We thank Professor R. Berndt for making his results[22] available to us. This work was supported directly by the Deutsche Forschungsgemeinschaft and by a fund through the Sonderforschungsbereich SFB 277.

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