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Thermally induced defects and the lifetime of electronic surface states

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The temperature-dependent linewidth of the $\bar{\Gamma}$ surface state on Al(100) was measured. The result cannot be reconciled, not even qualitatively, with the well-known model for describing the influence of electron-phonon coupling on the lifetime broadening on electronic surface states. It is argued that this is due to the presence of thermally excited defects on the surface. Incorporating this possibility into the analysis, the measured temperature dependence is found to be consistent with that expected from an *ab initio* calculation of the electron-phonon coupling strength. This phenomenon should be quite general and, indeed, a reanalysis of recently published data of Au(111) [S. LaShell *et al.*, Phys. Rev. B **74**, 033410 (2006)] resolves an apparent discrepancy between the measured and calculated electron-phonon coupling strengths.

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A detailed understanding of the lifetime of electronic states is at the very heart of current condensed matter physics. The interest in this is driven by several fields, such as the dynamics of chemical reactions or high-temperature superconductivity. Electronic surface states have proven to be an ideal testing ground for understanding of lifetime effects, and great progress has been made over the past few years.[1] Prominent examples are the $\bar{\Gamma}$ surface states on the (111) surfaces of the noble metals and on Mg(0001), where the agreement between calculated and measured lifetimes at low temperatures was found to be very good.[2–4]

The situation is less well understood at elevated temperatures where the electron-phonon (*e-ph*) coupling becomes increasingly important in limiting the lifetime τ of the surface states. It is apparently well understood how to interpret the temperature-dependent lifetime in terms of *e-ph* coupling (for reviews see Refs. 5–7): In most studies, it is assumed that only the *e-ph* coupling leads to an appreciable temperature dependence of the lifetime broadening and other mechanisms such as electron-electron (*e-e*) and electron-defect (*e-d*) scattering are constant as a function of temperature. Using these assumptions, quantitative agreement between experimental data and *ab initio* calculations was achieved for Mg(0001), Cu(111), and Ag(111). Remarkably, this appears to fail for the Au(111) surface state. The *e-ph* coupling strength, expressed by the parameter λ, was found to be about three times stronger[8] than predicted by the type of calculations which work well for Cu(111) and Ag(111).[8–10] This is all the more surprising because experiment and calculations agree excellently on the low-temperature lifetime, to which the *e-ph* coupling also contributes significantly.[2,3]

In this Brief Report, we mainly discuss the case of Al(100) which supports a deeply penetrating surface state in a narrow gap as Mg(0001). Unlike for Mg(0001), the temperature-dependent linewidth $\Gamma = \hbar/\tau$ is inconsistent with the result expected from calculations. Indeed, the data cannot even be described qualitatively using the accepted model. We argue that the origin of this lies in the assumption of a temperature-independent electron-defect scattering contribution to the lifetime. While the defect scattering contribution as such may be independent of temperature, the concentration of defects certainly is not. Taking this into account permits an accurate description of the experimental data which are consistent with the temperature-dependent linewidth expected from our *ab initio* calculation. We also show that the effect described here should be a quite general one, and we will illustrate this by showing that it can resolve the aforementioned inconsistencies for Au(111).

The energy- and momentum-dependent *e-ph* coupling parameter λ is defined as the first inverse frequency moment of the so-called Eliashberg coupling function α^2F.[11] *Ab initio* calculations of α^2F and λ for the $\bar{\Gamma}$ surface state on Al(100) have been performed by using the density-functional perturbation theory and the PWSCF code,[12] taking both phonon emission and phonon absorption processes into account. The electron-ion interaction was described by a nonlocal norm-conserving pseudopotential generated following von Barth and Car.[12] The plane-wave basis-set cutoff was restricted to 16 Ry. A periodically repeated slab geometry of the fully relaxed Al(100) slabs of 11 atomic layers separated by seven atomic layers of vacuum was used to study the surface electronic structure, phonon spectrum, and *e-ph* interaction. The Brillouin-zone (BZ) integrations were performed using 45 special points in the irreducible BZ and the first-order Hermite-Gaussian smearing technique with a width of 0.02 Ry. The calculated $\lambda = 0.51$ for the $\bar{\Gamma}$ surface state is slightly higher than $\lambda = 0.43$ evaluated at the Fermi level E_F in bulk Al and it is higher by a factor of 2 than λ obtained in Ref. 10. This can be accounted for by the use of an Ascroft pseudopotential screened within the Thomas-Fermi approximation in Ref. 10: The Ascroft pseudopotential gives an accurate description of electronic structure of bulk Al at E_F but

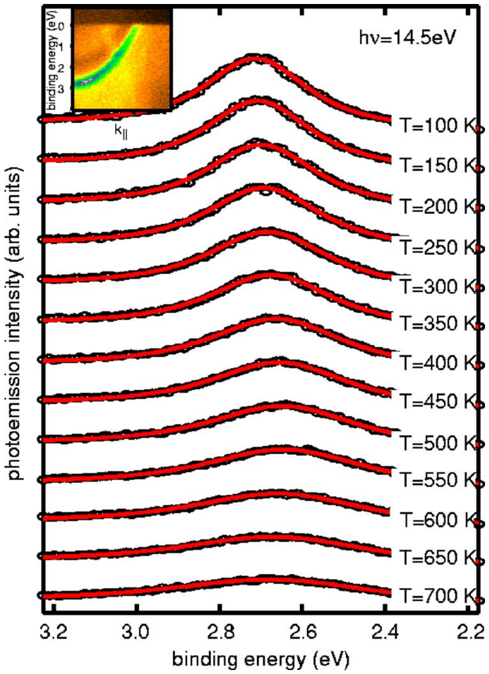

FIG. 1. (Color online) Temperature dependence of the surface state at $\bar{\Gamma}$. The measured data are the dots; the solid lines are fits to the data. The inset shows the dispersion of the surface state in the $\bar{\Gamma}$-$\bar{X}$ direction, measured at a photon energy of $h\nu$=67.5 eV.

it is less accurate for electron states far (2–6 eV) below E_F.

The surface was cleaned by cycles of Ar-ion bombardment at room temperature and at 673 K as well as annealing to 723 K. Initially, cleanliness was checked by Auger electron spectroscopy, in the later stages by traces of oxygen-related peaks in the valence band, and by the width of the surface state. Angle-resolved photoemission experiments were performed at the SGM-3 beamline of the synchrotron radiation source ASTRID in Aarhus.[13] The total energy resolution was set to 80 meV. The angular resolution of the analyzer is ±0.7°. The sample was cooled to approximately 30 K with a closed-cycle He cryostat. Measurements at higher temperatures were performed by heating the sample with the radiation from a filament mounted behind it. The filament current was chopped and the data were taken in the off-time of the duty cycle. Data were mostly taken for low photon energies around 14 eV where the photoemission cross section is resonantly enhanced due to the surface photoeffect.[14] Data taken at higher energies where the surface state cross section is enhanced due to its similarity to bulk X states[15,16] give similar results but the curve fitting of the spectra is more difficult due to the vicinity of bulk and surface peaks.

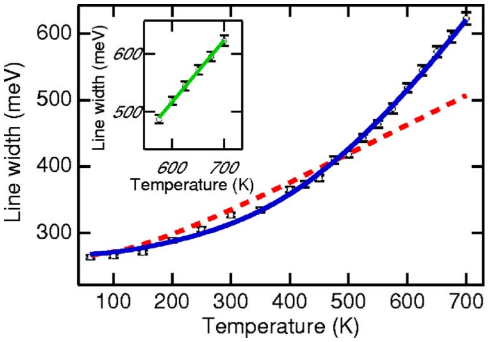

FIG. 2. (Color online) Temperature-dependent linewidth of the $\bar{\Gamma}$ surface state. The dashed line is a fit to Eq. (1). The solid line is a fit to the sum of Eqs. (1) and (3). The inset shows a fit to the high-temperature data only using Eq. (2).

Figure 1 shows the surface state peak at $\bar{\Gamma}$ as a function of temperature. The data are fitted with a Lorentzian peak on a linear background. The finite experimental resolution was taken into account by convoluting the Lorentzian line with a Gaussian. The resulting temperature-dependent linewidth is shown in Fig. 2. This linewidth Γ is assumed to be the sum of three contributions representing e-e scattering (Γ_{ee}), e-d scattering (Γ_{ed}), and e-ph scattering (Γ_{ep}). The first two are usually assumed to be independent of temperature. For Γ_{ee}, this is exactly true as long as the binding energy is large compared to k_BT and the band structure is independent of T. The role of Γ_{ed} will be discussed in detail below. If the *temperature dependence* of Γ is only due to Γ_{ep}, it can be described by

$$\Gamma = 2\pi\hbar \int_0^{\omega_{\max}} \alpha^2F(\omega')[1 - f(E-\omega') + 2n(\omega') + f(E+\omega')]d\omega' + \Gamma_0, \tag{1}$$

where E is the photoelectron binding energy (here, 2750 meV), ω' is the phonon energy, $\alpha^2F(\omega')$ is the Eliashberg coupling function, $f(\omega)$ and $n(\omega')$ are the Fermi and Bose-Einstein distribution functions, respectively, and Γ_0 is a temperature-independent offset which accounts for the combined effect of e-e and e-d scatterings. The integral extends over all phonon frequencies in the material. A derivation and detailed discussion of Eq. (1) is given in Ref. 17.

For $\alpha^2F(\omega')$, we assume a simple three-dimensional Debye model which is appropriate for such a deeply penetrating state.[4] This model contains two parameters, the Debye temperature Θ_D and the e-ph mass enhancement parameter λ. An effective Θ_D=573(180) K was determined from the calculated probability density of the surface-state wave function and the layer-resolved mean-square vibrational amplitude as determined by low energy electron diffraction.[18] The details of the procedure are the same as in Ref. 4.

The data in Fig. 2 are fitted to Eq. (1), and the result is shown as a dashed line. The agreement is quite poor. Moreover, the resulting value of λ=0.84(1) is significantly higher than the calculated value of 0.51. The reason for the discrepancy cannot lie in the incorrect description of the Eliashberg coupling function by our simple model, but it must be more profound: The high-temperature limit of Eq. (1), formally valid for $T \gg \Theta_D$, is a straight line with

$$\Gamma = 2\pi\lambda k_BT + \Gamma_0', \tag{2}$$

which is completely independent of the model used for the Eliashberg function. In practice, this limit is already reached at $T \approx \Theta_D/2$. If we limit the temperature range for the fit sufficiently, for example, to $T > \Theta_D/2$, the data can of course be fitted using a straight line. This is shown in the inset of Fig. 2. It leads to an unrealistically high λ of 1.8, in even worse agreement with the calculation.

A likely and simple explanation for these problems lies in the defect scattering component Γ_{ed} which has been taken as independent of temperature so far, as in many other studies which analyze electron-phonon coupling along the same lines (for some examples, see Refs. 19–25). A precise account of the temperature dependence of electron-defect scattering is complicated, since different types of defects will limit the lifetime in different ways. The important point, however, is that the number of defects should not be constant but follow an exponential behavior, depending on the activation energy of the defects E_a. We can take this into account by adding a term of the form

$$\Gamma_{ed} = Ce^{-E_a/k_BT} \tag{3}$$

to Eqs. (1) and (2), where C is a constant and E_a the activation energy for generating defects. We then fit the data to the sum of Eqs. (1) and (3). The result is an excellent fit, shown as a solid line in Fig. 2. In the fit, we have restricted the number of free parameters to Γ_0, C, and E_a. The value for λ has been taken from the calculation as being 0.51.

The results from the fit for C and E_a are 3.59(47) eV and 170(1) meV, respectively. C is a measure for how strongly the temperature-induced defects scatter electrons. It is difficult to relate C to a calculated value, but for E_a this is possible. We have studied the generation of defects on Al(100) by calculations of vacancy and adatom formation energies on a flat Al(100) surface, as well as at steps and kinks on terrace edges. The embedded atom method was used for the description of interatomic interaction potentials. The calculations show that at steps with kinks, the vacancy formation energy is as low as $E_a = 150$ meV, while at a flat surface, E_a is equal to 300–600 meV for vacancy and adatom formation energies.[26,27] A value $E_a = 150$ meV is in good agreement with the experimental result, confirming the qualitative interpretation of the data.

The temperature-induced formation of defects on surfaces should be a common phenomenon and it should have consequences for the determination of λ for many surfaces: If data points with small uncertainties are measured over a sufficiently large temperature range, the exponential increase of the linewidth will clearly reveal itself, resulting in a poor fit. If the temperature range is smaller, the fit might appear acceptable but the resulting λ will be too high.

In some cases, it may be possible to resolve apparent contradictions between calculated and measured values of λ. One example is the aforementioned case of Au(111). The data of LaShell *et al.*[8] for this surface state are shown in Fig. 3, together with a linear fit according to Eq. (2) also employed in their original work. Using a linear fit for Au appears highly reasonable due to the low bulk Debye temperature and the even lower surface Debye temperature.[28] Still, the line does not appear to fit the data especially well. Moreover, the resulting $\lambda = 0.33(1)$ compares poorly to the calculated value of 0.11.[10] The solid line in Fig. 3 shows a linear fit which assumes the theoretical $\lambda = 0.11$ plus an exponential term, i.e., the sum of Eqs. (2) and (3). The fit is very good, showing that the data are consistent with the calculated result for λ. The fit constants are $C = 0.238(31)$ eV and $E_a = 81(7)$ meV.

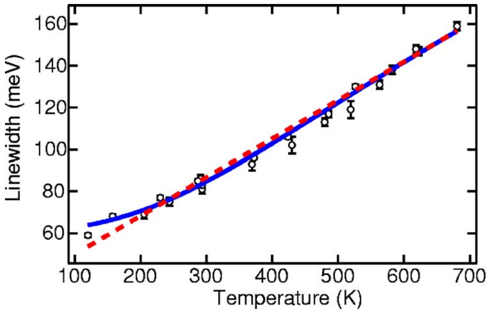

FIG. 3. (Color online) Temperature-dependent linewidth of the $\bar{\Gamma}$ surface state of Au(111), taken from Ref. 8. The dashed line is a fit to Eq. (2). The solid line is a fit to the sum of Eqs. (2) and (3).

The phenomenon of thermally excited defects and their influence on the lifetime of electronic states is well known from bulk transport properties where the resistivity of a bulk sample at a given temperature is affected by the number of defects in the sample. The number of defects can be increased by heating the sample to a high temperature and rapid quenching to low temperature. Such experiments give preexponential coefficients which are analogous to the constant C used here. In both cases, they describe how efficiently electrons are scattered from defects. In our experiments, C for Al was found to be much higher than C for Au. The same trend (a factor of 6) is found in the bulk measurements.[29,30] The very efficient scattering in Al explains why the effect is so strong on Al(100).

Having discussed the temperature dependence of the lifetime, a short comment on the linewidth extrapolated to zero temperature is appropriate. This value can be compared to the sum of the calculated contributions for electron-electron and electron-phonon scatterings. The difference between the two is ascribed to the presence of defects on the surface which are created during surface preparation, i.e., not the thermally generated defects. For the noble-metal surfaces, this difference can be very small.[2,3,10] If we extrapolate a fit to the data in Fig. 3 to zero temperature [using the full description of Eq. (1) instead of Eq. (2)], we get an experimental width of about 57 meV. This is significantly higher than the value of 21(1) meV stated in recent ultrahigh resolution work.[3] The difference is probably due to surface preparation and should not affect the resulting temperature dependence. This can be illustrated by comparing different temperature-dependent photoemission results for Cu(111) in which the absolute linewidth at a given temperature can be different but the resulting λ is unaffected by this.[19,20]

For Al(100), the extrapolated linewidth at 0 K is 267 meV. The calculated linewidth, Γ_{ee} (131 meV)+Γ_{ep} (35 meV), is 166 meV. Again, the difference of 101 meV is ascribed to defects which arise during surface preparation. Essentially, the same absolute linewidth was found after many preparations and on two different crystals, such that other reasons should also be explored. One possibility is related to the position of the surface state in a narrow gap which requires a fitting procedure using a background, rather than merely a Lorentzian peak. The precise choice of the function describing this background has an influence on the resulting absolute linewidth. Its influence on the temperature dependence is, however, negligible.

In conclusion, we have shown that thermally induced defects can have a significant influence on the temperature-dependent lifetime of electronic surface states. This can be a problem for the usual interpretation of temperature-dependent photoemission data in terms of electron-phonon coupling, which can only be identified when high-quality data are used. On the other hand, acknowledging this effect, disturbing inconsistencies between experiment and theory, as in the case of Au(111), can be resolved.

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