RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 19 15 MAY 1995-I

# Phonon contribution to quasiparticle lifetimes in Cu measured by angle-resolved photoemission

B. A. McDougall, T. Balasubramanian, and E. Jensen
*Physics Department, Brandeis University, Waltham, Massachusetts 02254*
(Received 13 March 1995)

The line shape of the photoelectron spectrum emitted from the $sp$-derived surface state at $\bar{\Gamma}$ on Cu(111) is investigated. The line shape is Lorentzian, and the temperature dependence of the width is linear, varying from 30 meV at 30 K to 75 meV at 625 K. Less than 5-meV variation with binding energy is observed. The temperature dependence is explained as the phonon contribution to the inverse hole lifetime, predicted to be $2\pi\lambda k_b T$ allowing the determination that the electron-phonon mass enhancement parameter $\lambda = 0.14 \pm 0.02$ for this surface state at $\bar{\Gamma}$. This is compared to $\lambda = 0.15$ reported as an average over the bulk Fermi surface.

In the standard picture of angle-resolved photoemission spectroscopy, the peak width observed from a perfect crystal with negligible dispersion of the hole state perpendicular to the surface is equal to the inverse hole lifetime $\hbar/\tau$.[1,2] A measurement of linewidth as a function of binding energy, temperature, and impurity concentration determines the dependence of the hole lifetime on these variables. If the measurements are done at hole energies relatively close to the Fermi energy $E_F$ then one can compare to determinations based on low-energy techniques, such as Fermi surface probes, conductivity, and specific-heat measurements. The photoemission measurement is in many ways superior to these other techniques. It is more direct, involves no Fermi surface averaging, and does not depend on assumptions about one-electron theory. Photoemission also has the unique advantage that the energy dependence of the lifetime is directly observable. Its well-known surface sensitivity of a few atomic layers is both an advantage and a disadvantage. On the one hand, surfaces can be studied, while, on the other hand, comparison with bulk sensitive techniques is complicated. Photoemission is also a complex many-body process, allowing some uncertainty about the degree to which the standard picture of identifying widths with inverse hole lifetimes is correct.[1,3–7] To date, there has been very little successful comparison of valence photoemission linewidths and inverse hole lifetimes, some notable failures of this identity, and some controversy.[3,5,8,9] We report here quantitative understanding of the temperature dependence of the linewidth of a Cu(111) surface state based on the phonon contribution to the hole lifetime. In addition, we describe a surface sensitive method of determining one of the most ubiquitous parameters of solid-state physics, $\lambda$, the electron-phonon mass enhancement parameter.

There are three processes that contribute to valence hole decay at zero temperature in metals. One is Auger decay, where one hole decays into two less tightly bound holes and an electron via the electron-electron interaction (electron-hole pair creation). The second is phonon scattering, where one hole decays into a less tightly bound hole plus a phonon via the electron-phonon interaction (phonon creation). The third is scattering by an impurity or defect from one momentum to another at fixed energy. At finite temperature, thermally generated excitations (phonons, electrons, and holes) participate in similar events. All three processes are thought to be well understood for bulk wide band metals, and quantitative calculations of the effect of each date from the 1960s.[10–12]

The results of the calculations are usually presented in terms of the electron self-energy. As long as the self-energy is only weakly dependent on energy and its imaginary component is small compared to the binding energy,[13] then the imaginary component of the self-energy $\Sigma_I = \hbar/2\tau$, the line shape is Lorentzian with full width at half maximum (FWHM) $W = \hbar/\tau$, and all contributions add linearly.[2] Existing calculations are for three-dimensional systems. Although metallic surface states are two dimensional in a one-electron sense, they are fully three dimensional as far as allowed decay modes are concerned. A surface state hole at parallel momentum $k_\parallel$ is degenerate with bulk two-hole, one-electron states with total momentum $k_\parallel$ as required for Auger decay, bulk one-hole–one-phonon states at $k_\parallel$ for phonon scattering, and bulk one-hole states for impurity scattering. Some numerical adjustment of the parameters used to characterize the decay processes in the bulk is expected in order to account for the different phonon and one-electron densities in the vicinity of the surface.

The Cu(111) $sp$-derived surface state has been extensively studied. It was first observed, to our knowledge, by Gartland and Slagsvold[14] in 1975, and has served as a prototype for the observation of several phenomena.[5,15–17] According to the present work, it has a maximum binding energy (at room temperature) of $E_0 = 390$ meV at $\bar{\Gamma}$, and disperses towards the Fermi level as $E_0 - E = 9380 k_\parallel^2$, with $E$ the binding or hole energy with respect to $E_F$ in meV, and $k_\parallel$ in Å$^{-1}$. This is very similar to the behavior reported by Kevan.[5] The Fermi momentum is 0.20 Å$^{-1}$ at room temperature. This is a small fraction of a surface reciprocal lattice vector (1.4–1.6 Å$^{-1}$), and no significant differences in dispersion are seen for the occupied states as the direction of $k_\parallel$ is varied.[5] The $\bar{\Gamma}$ binding energy is a linear function of temperature, with $dE_0/dT = -0.20$ meV/K, leading to a bandwidth of 440 meV at 30 K. Knapp *et al.*[15] observed a value for $dE_0/dT$ of $-0.27$ meV/K; they explain the shift as an effect of thermal expansion on the one-electron band structure. We believe that this is the correct explanation, and that our somewhat different numerical value is due to better experimental conditions. The surface state is closely related

 

to bulk states nearby in energy at the same $k_{\parallel}$.[16] The surface state at $\bar{\Gamma}$ is most closely related to the bulk $L$ point, while the surface state at $E_F$ is closely related to the bulk states just inside the Fermi surface neck perpendicular to (111). The entire surface-state band has a small energy on the scale of the bulk bandwidth ($<6\%$), and can be considered near in energy to $E_F$.

For bulk holes near $E_F$ in copper, the following is predicted. Auger decay contributes a term to the width of $W_{e\text{-}e}=2\beta[(\pi k_b T)^2+E^2]$.[10] Although $\beta$ is important for understanding effects such as the electronic contribution to the resistivity, it is small enough that it has not been measured for copper. Theoretical estimates are near 0.015 $eV^{-1}$, leading to $W_{e\text{-}e}\simeq 5$ meV at the bottom of the surface-state band, and temperature contributions below 1 meV for achievable temperatures.[18] Phonon scattering contributes $W_{e\text{-}p}=2\pi\lambda k_b T$.[12] This equation is formally valid independent of the form of the phonon spectrum at high temperatures for holes at $E_F$. It is expected to be reasonably valid to relatively low temperatures,[19] as can be seen in Fig. 1. The dependence of the phonon contribution on energy is more complex, and its determination requires some assumptions about the form of the phonon spectrum. The inverse lifetime can be calculated from the following formula:

$$\hbar/\tau(\omega,T)=2\pi\hbar\int_0^{\omega_{\max}} d\omega'\,\alpha^2F(\omega')[1-f(\omega-\omega')+2n(\omega')+f(\omega+\omega')],$$

where $\alpha^2F(\omega)$ is the Eliashberg coupling function and $f(\omega)$ and $n(\omega)$ are the Fermi and Bose-Einstein distributions.[12] In the Debye model, $\alpha^2F(\omega)=\lambda(\omega/\omega_D)^2$ for $\omega<\omega_D$, and zero elsewhere. Some representative results of integrating this formula in the Debye model are shown in Fig. 1. There is very little energy dependence of the phonon contribution to the width, until hole energies within the phonon band are reached. The temperature dependence is linear over most energies and most temperatures. A Debye energy of 27 meV, and a $\lambda$ of 0.15 was used.[12,20] Since the phonon spectrum only appears in an integrated form, these curves are reasonably valid for more realistic phonon spectra as well, as has been verified by numerical calculations. The impurity scattering contribution is proportional to the impurity concentration, but independent of temperature and binding energy; for the bulk, the magnitude of the effect is about 10 meV/%.[10,19]

The relevant results of all of this are simply stated. The Auger contribution is small, and its temperature dependence even smaller. The impurity and defect contribution is independent of temperature and binding energy, and expected to be important for typical degrees of surface cleanliness. The phonon contribution should be dominant at room temperature, and contribute nearly all of the temperature dependence. This dependence is linear for most achievable temperatures, with slope $2\pi\lambda k_b$. A measurement of the observed width versus temperature should yield an experimental determination of $\lambda$. Although expected to be dominant for modest binding energies, even at low temperatures, the phonon contribution has been virtually ignored in previous attempts to identify hole lifetimes with photoemission linewidths.[3,8,9]

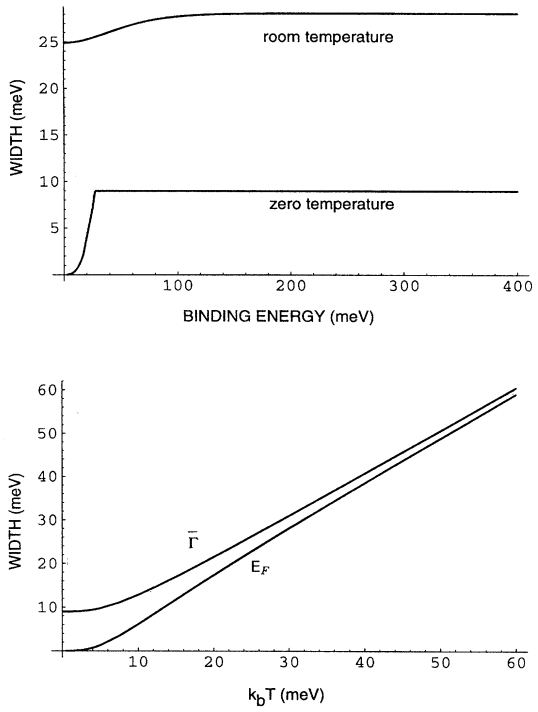


FIG. 1. Predicted phonon contributions to the full width of the peak (formally, twice the phonon contribution to the imaginary part of the electron self-energy) in the Debye model for $\lambda=0.15$ and $\omega_D=27$ meV. In the upper panel the width is plotted vs binding or hole energy at zero temperature and at room temperature. In the lower panel the width is plotted vs temperature at zero binding energy ($E_F$) and at the bottom of the band ($\bar{\Gamma}$), which occurs at 390 meV at room temperature and 440 meV at zero temperature.

There has been one published attempt to determine shallow hole lifetimes with adequate experimental resolution in energy and momentum.[5] The system chosen was the same Cu(111) $sp$ surface state that is the subject of this investigation. The width of the state as a function of binding energy at room temperature was measured. An increase from 55 meV FWHM at normal emission (maximum binding energy) to about 150 meV FWHM at $E_F$ was reported, after accounting for experimental resolution contributions. Negligible temperature dependence for temperatures below room temperature was reported. It is important to emphasize that these results cannot be explained by adjusting parameters in the theory described above; none of the three factors considered allow a decrease in hole lifetime as binding energy is decreased. These results were semiquantitatively explained as a nonlifetime consequence of impurity scattering from small amounts of surface defects and impurities. The imperfections permit nonconservation of $k_{\parallel}$ in the photoemission process, and broaden the peak proportional to its dispersion $dE/dk_{\parallel}$. This process contributes negligible width at the bottom of the band, but substantial width at the Fermi level, where the peak has large dispersion. It was argued that concentrations of imperfections in the unit atomic percentage range could account for the observed broadening.[5] We saw this effect in the preliminary stages of the work; it was eliminated by subsequent sample cleaning/annealing. Note that

this effect is quite distinct from the conventional impurity contribution to inverse lifetime discussed above.

The temperature dependence of valence linewidths has been studied by several authors.[21–23] A linear dependence of width on temperature for one metallic surface state has been reported, although not explained.[22] Studies on semiconductors have reported and explained linear temperature dependences of width on temperature in terms of phonon effects on hole lifetimes.[21,23]

The electron analyzer is a 50-mm mean radius hemispherical analyzer with $0.5\times5$ mm$^2$ entrance and exit slits, and $2\times20$ mrad$^2$ angle determining apertures. The nominal energy resolution is 10–15 meV. The experimental energy and angular resolution contribution to the observed widths is at most 5 meV. All reported widths are as observed, uncorrected for instrumental contributions. The ArI radiation, a doublet at 11.83 and 11.62 eV, is refocused by a SiC mirror to a spot on the sample of about 150 $\mu$m. Typical count rates are near 10 Hz. The Cu(111) sample is clamped in a strain-free manner onto a cartridge heater. The heater is mounted on a closed-cycle He refrigerator. The sample temperature can be varied between 30 and 900 K. The sample was cleaned by standard sputter-anneal cycles. Observed spectra are stable for hours at room temperature, while the width increases substantially in shorter times at low temperature due to the well-known increase in sticking coefficient at low temperatures. There is also substantial ($\simeq$10 meV) variation of width as a function of position on the sample. It is necessary at the beginning of the day to search for the spot on the sample that has the smallest width.

Figure 2 shows some representative data collected at normal emission. The two-peak structure is from the ArI doublet. Also shown are fit results. The fit function consists of two Lorentzian peaks plus a linear background. The background is always a small fraction of the peak height, and its variation across the spectrum is only marginally statistically significant. There are two important points to make about these data: the line shapes are Lorentzian within statistics, and the width increases with temperature. The Lorentzian shape encourages an interpretation based on hole lifetime. Off normal spectra (not shown) were slightly wider ($\leq$5 meV), with essentially the same temperature dependence as the normal emission spectra. The room-temperature spectrum is very similar in position and width to that reported by Kevan,[5] and substantially lower in width than that reported by Matzdorf *et al.*[22] The low-temperature and off-normal spectra have substantially smaller widths than those reported by either author.

Figure 3 shows peak widths from fits like those in Fig. 2 plotted versus temperature. The uncertainties indicated are statistical uncertainties from the fits. The straight line fit to the data has slope 0.074 meV/K, leading to $\lambda=0.14\pm0.02$. Measurements off normal (nearer $E_F$) show very similar behavior. This value for $\lambda$ can be compared with values in the literature derived from theoretical calculations, and from heat-capacity, electrical resistivity, and cyclotron resonance measurements for the bulk. Grimvall reports an average over the Fermi surface of $\lambda=0.15$,[12] which seems to be quite good agreement.

Closer analysis makes this apparent agreement a little less clear. $\lambda$ in the bulk shows substantial variation with position

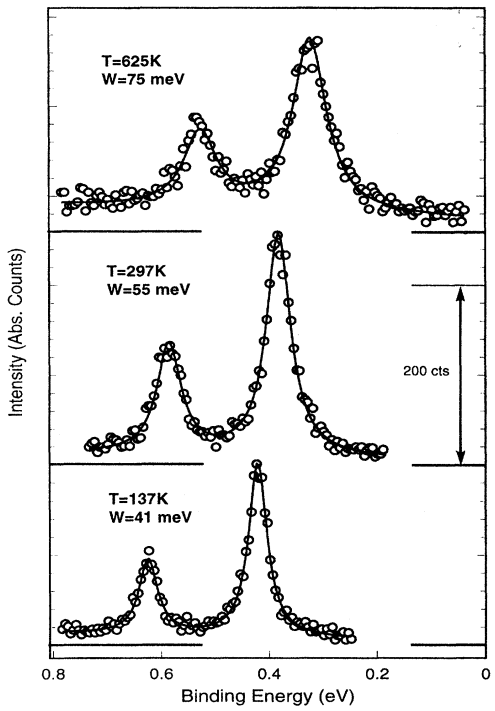


FIG. 2. Normal-emission ($\bar{\Gamma}$) spectra at three different temperatures. The 200-meV higher binding-energy satellite is from the Ar doublet. Data are open circles, while the solid line is a fit to (two) Lorentzian peaks with a linear background.

on the Fermi surface.[24,25] According to the analysis of experimental cyclotron masses by Lee,[25] $\lambda$ varies from 0.085 for the belly orbit perpendicular to the (111) direction to 0.23 for the neck orbit perpendicular to (111). Variation from 0.08 (belly) to 0.16 (neck) are reported by Khan *et al.*[24] from pure theory. As discussed earlier, the bulk Fermi surface states most like this surface state are those at the neck. If one compares the photoemission $\lambda$ (0.14) to the cyclotron neck $\lambda$ (0.22), there is substantial disagreement, while there is

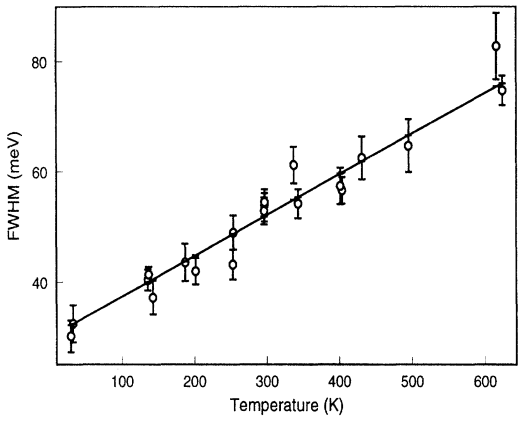


FIG. 3. Normal-emission peak widths from fits like those in Fig. 2, plotted vs temperature. Indicated error bars are statistical uncertainties from the fit. The solid line is a linear fit, with slope 0.074 meV/K, corresponding to $\lambda=0.14\pm0.02$.

good agreement with the pure theory neck $\lambda$ of 0.16. We believe that the photoemission and pure theory results are more likely to be correct. A difficulty with the cyclotron measurements is that $\lambda = m_{\rm obs}/m_0 - 1$, where $m_{\rm obs}$ is the observed mass and $m_0$ is the calculated bare mass. Because of the relatively small value of $\lambda$, uncertainties of 10% in either the cyclotron measurement or the bare mass calculation can be magnified to near 100% in the determination of $\lambda$. The photoemission measurement is much more direct and sensitive.

In spite of what seems to be a successful understanding of the temperature dependence of the photoemission linewidth, the net linewidth is not yet fully understood. Once $\lambda$ is known, theory includes only two remaining semiadjustable parameters for calculation of the normal emission widths: $\beta$, which characterizes the magnitude of Auger contributions, and the impurity lifetime contribution. The impurity momentum smearing, as described by Kevan, makes no contribution at $\bar{\Gamma}$.[5] From the lack of any observed decrease in width as the binding energy is decreased, it is known that $\beta$ is near to or smaller than the theoretical estimates, and that Auger decay plays little role in the observed width. The difference between the predicted normal emission width of about 30 meV at room temperature for a perfect crystal, and the observed width of 55 meV must be due to trace impurities and/or defects. A few percent impurity/defect concentration is required.

In conclusion, we have experimentally demonstrated that valence photoemission linewidths can be quantitatively understood as inverse hole lifetimes using known bulk parameters, that the dominant contribution to the hole lifetime typically comes from phonons, and that a surface value for the electron-phonon mass enhancement parameter $\lambda$ is easily derived from the temperature dependence of the observed linewidth.

This work was supported by NSF Grant No. DMR-9218706.

[1] N. V. Smith, P. Thiry, and Y. Petroff, Phys. Rev. B **47**, 15 476 (1993); N. V. Smith, Comments Condens. Matter Phys. **15**, 263 (1992).

[2] J. E. Inglesfield and E. W. Plummer, in *Angle Resolved Photoemission, Theory and Applications*, edited by S. D. Kevan (Elsevier, Amsterdam, 1992).

[3] Y. Hwu *et al.*, Phys. Rev. B **45**, 5438 (1992); **48**, 624 (1993).

[4] H. I. Starnberg, H. E. Brauer, and P. O. Nilsson, Phys. Rev. B **48**, 628 (1993).

[5] S. D. Kevan, Phys. Rev. Lett. **50**, 526 (1983); J. Tersoff and S. D. Kevan, Phys. Rev. B **28**, 4267 (1983).

[6] A. B. McLean, C. E. J. Mitchell, and I. G. Hill, Surf. Sci. **314**, L925 (1994).

[7] H. I. Starnberg and P. O. Nilsson, Surf. Sci. **287**, 776 (1993).

[8] C. G. Olsen *et al.*, Phys. Rev. B **42**, 381 (1992); Science **245**, 731 (1989).

[9] R. Claessen *et al.*, Phys. Rev. Lett. **69**, 808 (1992).

[10] D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (Benjamin, New York, 1969).

[11] S. Engelsberg and J. R. Schrieffer, Phys. Rev. **131**, 993 (1963).

[12] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, New York, 1981).

[13] These criteria are expected to be satisfied by all contributions except for the phonon contribution for hole energies near the Debye energy. See Ref. 11.

[14] P. O. Gartland and B. J. Slagsvold, Phys. Rev. B **12**, 4047 (1975).

[15] J. A. Knapp *et al.*, Phys. Rev. B **19**, 2844 (1979).

[16] S. G. Louie *et al.*, Phys. Rev. Lett. **44**, 549 (1980).

[17] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).

[18] J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958); **126**, 1453 (1962).

[19] P. B. Allen, Comments Condens. Matter Phys. **15**, 327 (1992).

[20] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rhinehart and Winston, New York, 1976).

[21] T. Grandke, M. Cardona, and L. Ley, Solid State Commun. **32**, 353 (1979).

[22] A. Goldman and R. Matzdorf, Prog. Surf. Sci. **42**, 331 (1993); R. Matzdorf, G. Meister, and A. Goldman, Surf. Sci. **286**, 56 (1993); **296**, 241 (1993).

[23] J. Fraxedas, M. K. Kelly, and M. Cardona, Phys. Rev. B **43**, 2159 (1991).

[24] F. S. Khan *et al.*, Phys. Rev. B **26**, 1538 (1982).

[25] M. J. G. Lee, Phys. Rev. B **2**, 250 (1970).