Nonquasiparticle structure in the photoemission spectra from the Be(0001) surface and determination of the electron self energy

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Complex structure in photoemission spectra of Be(0001) surface states near the Fermi energy is observed and explained as the effect of strong electron-phonon coupling. The weak momentum dependence of the electron-phonon contribution to the electron self energy Σ is exploited to determine Σ by direct inversion of the spectra.

The electronic structure of metals is often described in a quasiparticle picture. Low-energy electronic excitations consist of the promotion of electrons from occupied to unoccupied levels, creating two nearly independent quasiparticles, electron and hole. Each quasiparticle has a finite lifetime for decay, due to electron-electron, electron-phonon, and electron-impurity scattering. This picture leads to a simple description of most electronic processes. In particular, the angle-resolved photoemission (ARP) process for a single band of two-dimensional electrons (surface states or layered materials) is quite simple to describe: an incident photon creates an electron and a hole with net momentum zero and net energy equal to the photon energy. The emitted electron's energy and parallel component of momentum are measured. At each momentum value k, the energy spectrum consists of a single Lorentzian peak. The observed energy position of the peak at each momentum (referenced to the Fermi energy E_F) is the hole (quasiparticle) excitation energy E, while the width of the peak is the inverse lifetime of the hole excitation. A complete set of such spectra determine, and are typically presented in terms of the band structure $E(\mathbf{k})$ and lifetime $\tau(E)$. This picture has been quite successful in describing the ARP spectra of surfaces of many materials. Peak positions compare well with band calculations, while peak widths from high quality surfaces have been recently explained in terms of contributions from the electron-phonon and electron-impurity interactions.[1–4] The electron-electron interaction, as expected, makes negligible contribution to the widths of small binding energy peaks in wide band metals.[1]

In more interesting materials the quasiparticle picture is often invalid, and a more complex description of the electronic structure is required. In this case, the electron self energy $\Sigma(\omega,\mathbf{k})=\Sigma_R(\omega,\mathbf{k})+I\Sigma_I(\omega,\mathbf{k})$ is an important theoretical concept. Many quantities of interest can be calculated from $\Sigma(\omega,\mathbf{k})$, including the one-electron Green's function $G(\omega,\mathbf{k})=[\hbar\omega-\epsilon_{\mathbf{k}}-\Sigma(\omega,\mathbf{k})]^{-1}$, where $\epsilon_{\mathbf{k}}$ is the noninteracting one-electron energy. The band structure and lifetime no longer provide an adequate description of photoemission, and the photoemission spectrum can have quite complex structure. Under reasonable assumptions, the photoemission spectrum can be shown to be proportional to the hole spectral function $A(\omega,\mathbf{k})$ times the Fermi function.[5] The hole spectral function can be written in terms of Σ as

$$A(\omega,\mathbf{k})=\frac{\pi^{-1}|\Sigma_I(\omega,\mathbf{k})|}{[\hbar\omega-\epsilon_{\mathbf{k}}-\Sigma_R(\omega,\mathbf{k})]^2+\Sigma_I(\omega,\mathbf{k})^2}. \tag{1}$$

Hole energies $\hbar\omega$, not to be confused with the photon energy, are negative and measured from the Fermi energy E_F. In the limit that Σ is small and slowly varying, this description reduces to the quasiparticle picture, with $\hbar/2\Sigma_I\rightarrow\tau$ and $\epsilon_{\mathbf{k}}+\Sigma_R\rightarrow E(\mathbf{k})$. Nonquasiparticle (NQP) behavior is expected even for wide band metals when electron-phonon coupling is strong.[6] Such systems are important to study because they are the simplest to exhibit NQP behavior. Very recent work on the Be(0001) system reports NQP behavior very similar to that shown here.[7]

Even though the self energy plays a prominent role in the description of many physical properties, it has not been directly accessible to experiment. When the quasiparticle picture is valid, Σ_I can be determined from the width of the peak in the ARP spectrum,[1–4] and Σ_R from the difference between the observed peak position and that predicted by band calculations.[4] In more complex situations there has been some success in determining Σ by exploiting the relation between the spectral function and the imaginary part of the Green's function.[8] We show here a simple method to directly invert ARP spectra to find Σ without any assumptions about the phonon spectra other than weak momentum dependence of electron-phonon coupling.

The electron-phonon contribution to the self energy is effectively independent of momentum, $\Sigma(\omega,\mathbf{k})\rightarrow\Sigma(\omega)$, and at zero temperature can be written

$$|\Sigma_I(\omega)|=\pi\hbar\int_0^{|\omega|}\alpha^2F(\omega')d\omega', \tag{2}$$

where $\alpha^2F(\omega)$, the Eliashberg coupling function, is the phonon density of states weighted by electron-phonon coupling.[9] Σ_R is the Hilbert transform of Σ_I. A convenient model for $\alpha^2F(\omega)$ is the isotropic zero temperature Debye model (phonon energy proportional to wave vector) with constant electron-phonon interaction matrix element. The system is

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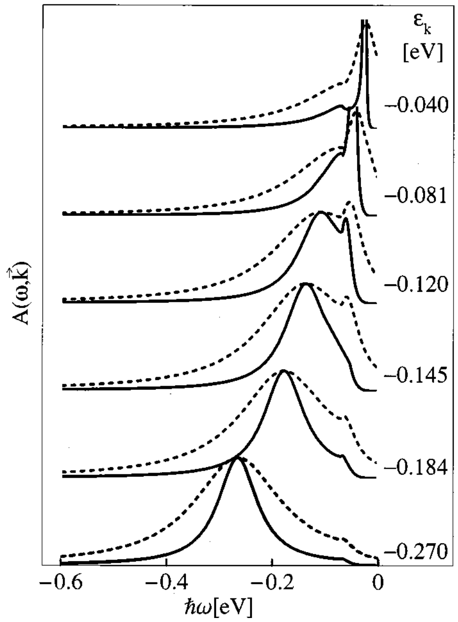

FIG. 1. Spectral function in the Debye model for $\omega_D = 65$ meV and $\lambda = 0.65$ with (dashed) and without (solid) a constant 54 meV added to Σ_I to represent impurity scattering.

then characterized by only two parameters, the dimensionless mass enhancement parameter λ representing the strength of the electron-phonon interaction, and the Debye energy ω_D, or maximum phonon energy. $\alpha^2F(\omega) = \lambda(\omega/\omega_D)^2$ for $\omega < \omega_D$ and zero otherwise. In this approximation

$$|\Sigma_I(\omega)| = \hbar\lambda\pi|\omega|^3/(3\omega_D^2), \quad |\omega| < \omega_D,$$

$$|\Sigma_I(\omega)| = \hbar\lambda\pi\omega_D/3, \quad |\omega| > \omega_D \tag{3}$$

$$\Sigma_R(\omega) = -(\lambda\hbar\omega_D/3)\times[(\omega/\omega_D)^3 \ln|(\omega_D^2-\omega^2)/\omega^2| + \ln|(\omega_D+\omega)/(\omega_D-\omega)| + \omega/\omega_D].$$

The spectral function $A(\omega,\mathbf{k})$ for this model is shown in Fig. 1, using parameter values $\lambda = 0.65$ and $\omega_D = 65$ meV, chosen to yield good agreement with the data to be presented below. The effect on $A(\omega,\mathbf{k})$ of adding a constant 54 meV to Σ_I (to represent impurity scattering, again chosen to match the experimental data below) is also shown.

This simple model illustrates semiquantitatively the interesting effects expected of real strongly coupled electron-phonon systems in the non-superconducting state. There are quasiparticle peaks at ϵ_k large and small compared to ω_D, strongly NQP structure for ϵ_k near ω_D, and additional NQP structure for many values of ϵ_k for ω near ω_D.

If one assumes negligible momentum dependence of Σ, then the inversion of the spectral function is simple: Eq. (1), rewritten to emphasize the momentum independence of Σ becomes

$$A_\omega(\epsilon_k) = \frac{\pi^{-1}\Sigma_I(\omega)}{[\hbar\omega - \epsilon_k - \Sigma_R(\omega)]^2 + \Sigma_I(\omega)^2}. \tag{4}$$

At fixed ω, $A_\omega(\epsilon_k)$ describes simple lorentzian curves with position $\tilde{\epsilon}_k = \hbar\omega - \Sigma_R(\omega)$ and full width $2\Gamma = 2\Sigma_I(\omega)$. A fit of the photoemission intensity vs ϵ_k to lorentzian curves directly yields $\Sigma_I = \Gamma$ and $\Sigma_R = \hbar\omega - \tilde{\epsilon}_k$.

Σ can have non-negligible momentum dependence in two distinct ways. If the system is anisotropic, as is common for complex Fermi surfaces, Σ is manifestly not independent of momentum. However, the energy dependence should still dominate the momentum dependence of the electron-phonon contribution to $\Sigma(\partial\Sigma/\partial\hbar\omega \gg \partial\Sigma/\partial\epsilon_k)$ unless the direction in momentum space is nearly parallel to the Fermi surface. This analysis is again valid, and should be performed for several cuts in momentum space perpendicular to the Fermi surface, generating the full $\Sigma(\omega,\mathbf{k})$. If Σ has significant electron-electron contribution, or if the system is superconducting, then the assumption of weak dependence of Σ on ϵ_k fails and the analysis is inappropriate.

Be(0001) is the proper system for experimental observation of these effects because of the existence of a well defined surface state at and near the Fermi energy, strong electron-phonon coupling, and a very large phonon energy scale. This system has been previously studied by lower resolution ARP,[10] by scanning tunneling microscopy[11] and by electronic structure calculation,[12] and is well understood. Although electron-phonon coupling is weak in the bulk, the surface states increase the electronic density of states at the Fermi energy and thus electron-phonon coupling at the sample surface.[2]

Data from Be(0001) were taken at a temperature of 40 K along a line in momentum space perpendicular to the Fermi surface in a direction midway between $\overline{\Gamma}-\overline{K}$ and $\overline{\Gamma}-\overline{M}$. The data were taken with Ne resonance radiation (16.85 and 16.67 eV), with the 16.67 eV contribution (approximately 25%) removed for presentation and analysis. Energy resolution is near 15 meV, and momentum resolution is 0.008 Å^{-1}; these contribute negligibly to the data, except very near to the Fermi energy.[13] Peak count rates were near 4 Hz. The data were acquired in the conventional manner, intensity vs. energy at fixed angle. Some data are presented in this form in Fig. 2. The complex shape of these spectra for ϵ_k near 100 meV clearly shows that a quasiparticle description is inadequate. There is substantial similarity to the model spectra of Fig. 1.

Some of the data are re-plotted at fixed ω vs ϵ_k in Fig. 3, together with Lorentzian fits. As expected, because of the weak dependence of Σ on momentum, the spectra are much simpler when viewed in this manner.[14] Following the analysis procedure described above, the fit results for the full data set are presented as $\Sigma_I(\omega)$ and $\Sigma_R(\omega)$ in Fig. 4, together with the Debye model calculations of Eq. (3) for $\lambda = 0.65$ and $\omega_D = 65$ meV, and with Σ_I offset by 54 meV. This offset is attributed to impurity scattering, and corresponds to a mean free path of 47 Å, indicating good surface quality. The data points in Fig. 4 are statistically independent so that the significance of possible structure can be estimated from the data scatter.

Neither isotropy nor any particular model for $\alpha^2F(\omega)$ is assumed in this analysis: the only free parameter is ϵ_k. For the small range of k near $k_F = 0.943$ Å^{-1} studied, ϵ_k should be nearly linear, and not too different from a k_F linearization of the calculated nearly free electron parabola $\epsilon_k(\mathrm{eV}) = 5.8(k-k_F)(\text{Å}^{-1})$.[12] We analyzed the data iteratively, starting with this function, varying it to force Σ_R to zero at

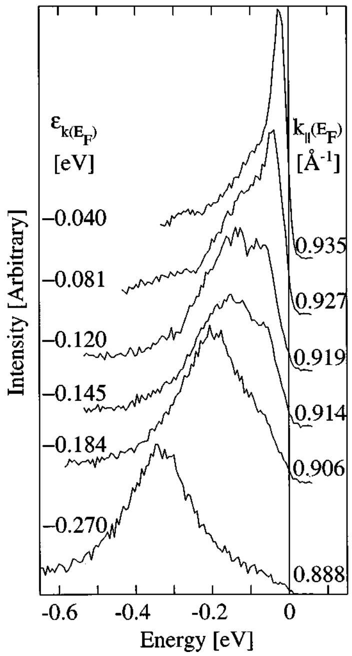

FIG. 2. Photoemission spectra at fixed angle, intensity vs energy. Non-quasiparticle structure is visible in the three spectra with largest momenta. The Fermi momentum is 0.943 Å^{-1}. The momenta and ϵ_k quoted are calculated at the Fermi energy and vary slightly across each spectrum. The functional form chosen for ϵ_k is discussed in the text.

$\omega=0$ and approach zero as $\omega\rightarrow-\infty$. We find that $\epsilon_k=5.15(k-k_F)+4.0(k-k_F)^2$ works well, and use this function in our presentation. The shape of the experimental Σ_I does not change unless ϵ_k becomes highly nonlinear (although it scales with $\partial\epsilon_k/\partial k$), while the shape of Σ_R depends more sensitively on the function ϵ_k.

Both the experimental Σ_R and Σ_I are similar to the model calculations: Σ_I increases rapidly from its $\omega=0$ value, and saturates at a value of 95 meV for $|\hbar\omega|>70$ meV, while Σ_R rises linearly from a value near zero at $\omega=0$, peaks near $|\hbar\omega|=60$ meV, and then drops back to zero. The mass enhancement parameter is defined by $\lambda=-\partial\Sigma_R(\omega)/\partial\hbar\omega|_0$ but is difficult to evaluate for these data. The main difficulty is to measure the slope near enough to $\omega=0$ that it is a good approximation to λ, but to include enough points that the determination is statistically significant. There are also resolution issues,[13] and sensitivity to the assumed ϵ_k. Values of the slope from 0.6 to 0.8 can be obtained, so we quote $\lambda=0.7\pm0.1$. The best fit to the Debye model uses $\lambda=0.65$ and $\omega_D=65\,\mathrm{meV}$.

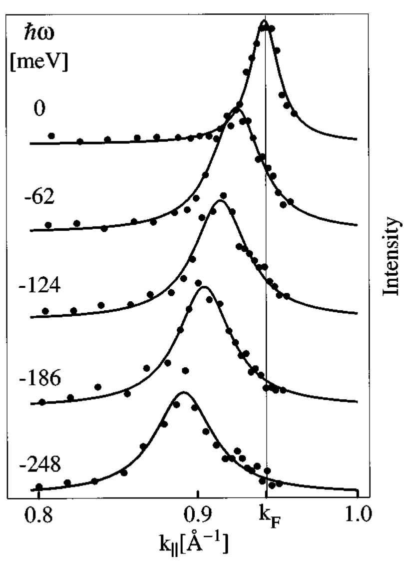

FIG. 3. A re-presentation of some of the data used in Fig. 2 at fixed energy, intensity vs electron momentum. The weak momentum dependence of Σ is demonstrated by the quality of the lorentzian fits (solid lines).

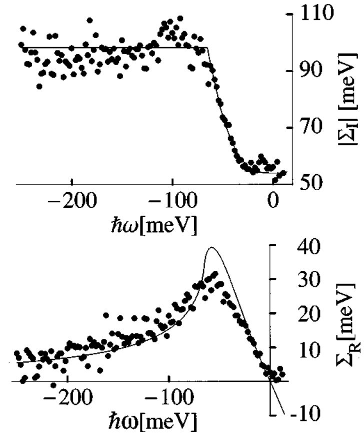

FIG. 4. $\Sigma(\omega)$ determined by fitting the full data set to lorentzian curves as in Fig. 3, as described in the text. The solid curves are Debye model Σ for $\lambda=0.65$ and $\omega_D=65\,\mathrm{meV}$.

This value for $\omega_D=65\,\mathrm{meV}$ is substantially lower than the bulk value of 80 meV, consistent with a calculation of surface phonon energies.[15] $\lambda=0.7\pm0.1$ is substantially smaller than the value of $\lambda=1.15\pm0.1$ found by Balasubramanian, Jensen, Wu, and Hulbert[2] (BJWH) and $\lambda=1.18$ found by Hengsberger *et al.*[7] in photoemission studies of the same surface state. BJWH determine λ from the temperature dependence of the width. Most of the discrepancy with BJWH is a technical error in their analysis. Since their data were taken at fixed angle, the momentum varied through the spectrum. This is known to distort the spectrum, and in the case of quasiparticle structure near k_F, increase observed widths by a factor $(1-mv_F\sin^2\theta/\hbar k_F)^{-1}$, where m is the electron mass, v_F is the Fermi velocity, and θ is the photoelectron exit angle.[16] Because of the large v_F of this state and the low-photon energy used by BJWH, this correction factor is a surprisingly large 1.32: their corrected λ becomes 0.87. The remaining discrepancy is probably due to the fact that BJWH used the bulk value (80 meV) for $\hbar\omega_D$ in their analysis, rather than the lower surface value of 65 meV. Hengsberger *et al.* determine λ from the renormalization of the dispersion near E_F. We believe that their determination is in error because they use peak positions too far from E_F (as large as 35 meV) in their determination of the renormalized dispersion. We find, using Debye model simulated spectra including an impurity contribution, that this can result in substantial overestimation of λ.

There are some interesting differences between the experimental and Debye model Σ in Fig. 4. Since Σ_I is the integral of a positive definite function, extrema are not allowed.[17] Peaks somewhat larger than can be accounted for statistically are visible in the experimental Σ_I curve near 10 and 100 meV: they could be evidence of the breakdown of this analysis, or of peaks in the electronic density of states, which was assumed constant in the derivation of Eq. (2). The peak in Σ_R is not as large as that of the model calculation: this is probably explained by the non-Debye shape of $\alpha^2F(\omega)$ in the surface layer.[15] Finally, the behavior of Σ_R near to and above $\omega=0$ appears to deviate somewhat from the calculation. This is an artifact of the energy resolution.[13]

There has been speculation that this surface would exhibit surface superconductivity, which might have a large energy gap.[2] We see no evidence of a superconducting gap larger than 5 meV at this temperature and level of surface perfection, in agreement with Hengsberger *et al.*[7] However, our mean free path of 47 Å though larger than that observed in other recent studies, may still permit the scattering of surface states pairs into the bulk rapidly enough that superconductivity is destroyed.[2,7]

In summary, we have observed NQP behavior in the photoemission spectra from Be(0001) surface states. We have shown that the observed behavior is consistent with that expected for strong electron-phonon interaction. We have also shown that the spectra can be inverted to yield an experimental determination of the electron self-energy.

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[13] When the energy resolution is larger than kT and $\omega \simeq 0$ the effective analysis energy is pulled down from its nominal value by the strong energy dependence of the Fermi factor. In the determination of Σ_R, the peak position $\tilde{\epsilon}_k$ is subtracted from the nominal analysis energy. Since the nominal energy is larger than the effective energy, the resulting Σ_R is too large.

[14] Because ϵ_k and k are nearly proportional, there is no quantitative distinction between fitting in k space or in ϵ_k space.

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[17] Equation (2) can be trivially inverted, yielding $\alpha^2F(\omega) = (\pi\hbar)^{-1}\partial\Sigma_I(\omega)/\partial\omega$, suggesting that ARP data with better statistics than these could be used to measure $\alpha^2F(\omega)$.