2. Particle in a box: quantization and phase shift

The surface photoemission term discussed earlier gives rise to emission from surface states, bulk states, quantum well states, etc. as long as the states have a finite amplitude at the surface. With appropriately chosen photon energies, the results are basically the angle-resolved local density of states at the surface. For thin films, quantum well states are often the dominant features.

The simplest model for a thin film is just a quantum box. Let us consider a one-dimensional infinite box as shown in Fig. 28. The wave vector $k$ is quantized to be $n\pi/D$, where D is the width of the box. This follows from solving the Schrödinger equation under the constraint of the boundary condition (zero amplitude at the two boundaries). The quantum number $n = 1, 2, 3, ...$.

How about $n = 0$? The wave function, given by $\sin(kz)$, is identically zero. So, $n = 0$ can be excluded. What about negative values of $n$? Since $\sin(kz) = -\sin(-kz)$, these do not correspond to new states. Thus, all distinct, nontrivial states are given by $n = 1, 2, 3, ...$. A note of caution: sometimes the counting of the quantum number begins with $n = 0$. It depends on the problem being considered.

The quantized states, or quantum well states, are just standing waves in the box. The energy of the particle is $\frac{\hbar^2 k^2}{2m}$. The energy spacings between neighboring states diminish for increasing $D$ (film thickness).

![Fig. 28](image)

Quantum well states in Ag(111) films grown on Si(111) seen in normal emission

Sample quality a major issue
Low temperature deposition + annealing yields a good film
More QWS for thicker films
Projected density of states at surface
$\rho(E, k, z = 0) = \sum_{i} |\langle k, z = 0 | \phi_i \rangle|^2 \delta(E - E_i)$
Very thick film $\rightarrow$ QWS merge $\rightarrow$ indirect transition continuum (bulk band structure)

![Fig. 29](image)
Shown in Fig. 29 are normal emission data taken from Ag films grown on Si(111)-(7x7). The bottom spectrum is for a 30 Å film deposited at 100 K. One sees a featureless spectrum with a Fermi edge at zero binding energy. The film is disordered, and the spectrum is roughly the Ag density of states in 3D. The sharp rise near 4 eV binding energy corresponds to the onset of the Ag 4d states.

Upon annealing to 300 K, the film orders to form a Ag(111) structure in parallel epitaxy with respect to the substrate. Peaks emerge in the spectra, which correspond to quantum well states, except for the first one near the Fermi level, which corresponds to the Ag(111) Shockley surface state mentioned earlier.

Upon deposition of 4 Å of Ag on this film for a total thickness of 34 Å, the quantum well peaks disappear. They reappear after annealing. The data show that the quantum well peaks become more crowded at larger film thicknesses. This behavior is expected as the energy spacings between neighboring quantum well states should diminish. When the film gets really thick, the quantum well peaks should merge and turn into the indirect-transition band continuum discussed earlier for single crystal Ag(111).

The infinite quantum box is a crude approximation for actual films. Electron propagation in a solid is governed by the band structure. Shown in Fig. 30 is the band structure of Ag. The direction of interest is the [111] direction from $\Gamma$ to $L$.

Consider, for simplicity, a one-dimensional, single-band model. One atom corresponds to one state; two atoms, two states; and so on. A chain with $N$ atoms should have $N$ states. When $N$ is very large, these $N$ states form a nearly continuous band; their wave vectors form an equally spaced set spanning the first Brillouin zone. The exact placement of the set of wave vectors relative to the zone center can depend on the assumed boundary condition.

The above model can be generalized to films. For a film with $N$ atomic layers, there are $N$ distinct $k_\perp$ values along the perpendicular direction within the first Brillouin zone. In other words, each bulk band should correspond to $N$ quantum well states. The quantization of the wave vector is schematically indicated in the figure with vertical lines.

Each quantum well state can have a finite $k_\parallel$ (parallel component of the momentum). The energy dispersion gives rise to a subband. The subband dispersion relations can be mapped out straightforwardly by angle-resolved photoemission.
Fig. 31

The first equation in Fig. 31 is the quantization condition for a free particle confined in an infinite well in 1D. Thin films do not have infinite barriers at the boundaries. With a periodic crystal potential and for an arbitrary boundary condition, it is better to use the Bohr-Sommerfeld quantization condition as shown. Here, \(2k_n D\) is the geometric phase shift associated with a round trip in the well; \(\phi_1\) and \(\phi_2\) are the reflection phase shifts at the two boundaries. These add up to \(2n\pi\) in order to form a standing wave (constructive interference condition). \(k_n\) here should be understood as the Bloch wave vector associated with the periodic crystal potential. As will be shown later, this quantization condition comes from solving the Schrödinger equation.

While both quantization conditions use \(n\) for the quantum number, they actually differ by one. As will be shown later, the quantum number \(n\) in the Bohr-Sommerfeld condition generally begins with 0. In other words, \(n = 0, 1, 2, \ldots\) Sorry for the confusion. One could rectify the situation by using \((n - 1)\) in place of \(n\) in the Bohr-Sommerfeld condition, and so \(n\) begins with 1. But we will use the conventional form of the Bohr-Sommerfeld condition.

\[
k_n = \frac{n\pi}{D}
\]

for a free particle in a box; \(n = 1, 2, 3, \ldots\)

More generally, Bohr Sommerfeld quantization rule, or phase accumulation model:

\[
2k_n D + \phi_1 + \phi_2 = 2n\pi
\]

Total round trip phase shift is \(2n\pi\), standing wave condition.

\(\phi = \) boundary phase shift (at surface and interface)

Note: this \(n\) is not the same \(n\) as before (sorry for the confusion!)

Related question: what is the meaning of \(\phi\)?

---

Fig. 32
This confusion has to do with the boundary phase shifts. Consider a simple 1D model: an electron with energy $E$ impinges upon a potential step of magnitude $V$ at $z = 0$ as shown in Fig. 32.

The incident wave is $\exp(ikz)$. It is (partially) reflected by the potential step. The reflection coefficient $r \exp(i\phi)$ is generally complex. $r^2$ is the reflectivity; it equals unity if $E < V$ (100% reflection). $\phi$ is the phase shift upon reflection.

The diagram at the bottom of Fig. 32 shows the total accumulated phase of the particle as it travels. It is $kz$ before hitting the boundary. After reflection, it receives a boost of $\phi$ at the boundary. As the particle travels backward toward $-z$, it accumulates additional phase shift of $-kz$, where $z$ becomes increasingly more negative.

This 1D problem can be solved exactly to yield the reflection coefficient as a function of $EV$. Here, $E \geq 0$, but $V$ can be positive (step up) or negative (step down). The results are shown in Fig. 33.

A very small positive $EV$ corresponds to an infinite step up. The phase shift is $-\pi$, and $r = 1$ based on the calculation. In other words, the reflection is 100% and causes a phase reversal. The incident and reflected waves add up to zero at the boundary, as should be (because the wave cannot penetrate an infinite wall, the amplitude must be zero at the boundary). One might think that a phase shift of $+\pi$ could also be a good choice. However, the case of a very small positive $EV$ actually has a phase shift slightly larger than $-\pi$ (see the calculation), if we insist that the phase shift must be chosen between $-\pi$ and $+\pi$. Analytic continuation stipulates that we must choose $-\pi$ for the limiting case.

The phase shift increases as the particle energy increases, and the reflectivity remains unity until the energy of the particle equals the barrier height. For energies above the barrier height, the phase shift becomes zero, independent of the particle energy, and the reflectivity drops rapidly.

The readers are encouraged to examine the trends for negative $V$.

Let us return to the Bohr Sommerfeld condition. Consider a quantum box with two infinite walls. The phase shift at each wall is

$$2k_nD + \phi_1 + \phi_2 = 2n\pi$$

For a box, $\phi_1 = \phi_2 = -\pi$. $2k_nD = 2(n+1)\pi$ $k_n = \frac{(n+1)\pi}{D}$

However $k_n = \frac{n\pi}{D}$ for a free particle in a box with $n = 1, 2, 3, \ldots$

So, $n = 0, 1, 2, 3, \ldots$ for $2k_nD + \phi_1 + \phi_2 = 2n\pi$

Unfortunate confusion!

Always asking - do the quantum numbers begin with 0 or 1?

There are other confusing issues.

One could use $2k_nD + \phi_1 + \phi_2 = 2(n - 1)\pi$ with $n = 1, 2, 3, \ldots$

Your choice of the definition! One might be better than the other.
− π (not π or zero). As shown by the derivation given in Fig. 34, the quantum number \( n \) based on the Sommerfeld condition is indeed different from that in the usual formula \( k_n = \frac{n\pi}{D} \) by unity.

This unfortunate confusion results from two different conventions. However, as long as one keeps track of the assumptions, there should not be a problem.

**Exercises for you:**

1. Phase shift for a plane wave incident on a material with a simple gap (Shockley inverted or non-inverted).
2. Phase shift between two materials, each with a gap.
3. Use VASP (or any other schemes) to calculate phase shifts for a free standing metal film (in vacuum).
4. ...

Hint: phase for a Bloch state (Bloch phase):

\[
\psi = u(z) \exp(ikz) + r \exp(i\phi) u(-z) \exp(-ikz)
\]

where \( u \) is a periodic function.

For a film, the dispersion relation \( E(k) \) is that for the solid.

Fig. 35

The above discussion in terms of a free electron and sharp potential steps can be readily generalized to the case of a solid film. The dispersion relation \( E(k) \) is replaced by the actual band structure. The phase shift must be defined in terms of the Bloch waves in the solid instead of plane waves; see the equation given.

Several exercises are suggested in Fig. 35. The readers are encouraged to perform the calculations to gain a deeper understanding of the phase shift function under various scenarios.

**Ag on Au(111)**

Discrete states for Ag on Au up to \( \sim 1.1 \text{ eV} \)

Evolve toward band edge at larger thicknesses

No such states for Au on Ag

![Graph showing binding energy and intensity for Ag on Au(111)](image)

Fig. 36
The old results presented in Fig. 36 for Ag(111)/Au(111) illustrate nicely some key features of the electronic structure of thin films. Ag and Au have a good lattice match and their band structures along [111] are very similar except for an offset in energy.

On the left, the four normal emission spectra are from Au(111) + 20 ML Ag, Ag(111), Ag(111) + 20 ML Au, and Au(111). The Au(111) + 20 ML Ag case shows the Ag(111) Shockley surface state and three quantum well states ($\nu = 1, 2, \text{and} 3$). The spectrum from single-crystal Ag(111) shows the same surface state, but not the quantum well states. Both Ag(111) + 20 ML Au and Au(111) show the Au(111) Shockley surface state; no quantum well states are observed.

The data on the right shows the thickness dependence of the quantum well states as a function of Ag film thickness on Au(111). The quantum well states converge toward the sp band edge for increasing film thicknesses as expected. The quantum number $\nu = 1, 2, \text{and} 3$ will be explained later. The surface state can be assigned as $\nu = 0$ by analytic continuation.

There is an apparent threshold for quantum well states at $\sim 1.1$ eV binding energy. Quantum well states are seen only at lower binding energies. Another interesting observation is that the complementary system, Au on Ag(111), shows no quantum well states. These observations will be explained next in terms of the Ag and Au band structures.

![Confinement - Quantum Well States](image)

On the left in Fig. 37 is the Ag band structure. The region of interest is indicated by a circle. This portion of the band structure is shown in detail on the right, together with the band structure of Au, which has a lower energy. The band edge of Ag is at $\sim 0.3$ eV, while the band edge of Au is at 1.1 eV.

Electrons in Ag at energies above 1.1 eV binding energy are confined by the Au band gap. So, between 0.3 and 1.1 eV, quantum well states are expected for Ag films on Au(111). Indeed, the data show a threshold of about 1.1 eV for the quantum well states. At energies below 1.1 eV, Ag electrons are not confined, but the potential step leads to partial reflection at the Ag-Au boundary. This partial reflection allows the formation of quantum well resonances, which can be regarded as "leaky" or damped quantum well states. The amplitude of the electron wave diminishes upon each reflection at the Ag-Au boundary; this damping leads to a shorter lifetime and a correspondingly wider peak width. Evidence for such resonance states can be found in the data.

For Au films on Ag(111), the electrons in the Au are not confined, and no quantum well states are expected or observed.

The surface states in Ag and Au have fairly short penetration depths. For the 20 ML film thickness employed in the experiment, the surface state in the Ag film or Au film is not affected by the presence of the interface. Thus, its binding energy is similar to the corresponding single-crystal case. At smaller film thicknesses, the surface state energy can
shift. Measurements of the energy shift as a function of film thickness can yield the penetration depth of the surface state.

\[
\text{QWS in Ag(111) films are near the band edge at L. Convenient to measure } k \text{ from L.}
\]
\[
2k'\pi t + \Phi = 2n\pi \quad \text{with } k \text{ measured from the zone center.}
\]
\[
k' = \sqrt{3\pi/a - k}
\]
\[
2k'\pi t - \Phi = 2(N - n)\pi = 2\nu\pi
\]

The sign for the phase is reversed! The quantum number is also redefined (but one often uses the same \(n\) notation!). Peaks labeled by \(\nu\) seem* to evolve continuously for varying \(N\). Labeling by \(n\) is inconvenient here.

*Discrete peak movement for distinct film thicknesses \(N\).

Figure 38 is an explanation for the quantum number \(\nu\) for the Ag films grown on Au(111). As mentioned earlier, we assign \(\nu = 0\) to the surface state and 1, 2, ... to the quantum well states. The region of interest is very close to the band edge near the L point at the Brillouin zone boundary.

As shown in the slide, we begin with the Bohr-Sommerfeld quantization condition with \(k\) measured from the zone center, where \(t\) is the monolayer thickness and \(a\) is the lattice constant of Ag. Since the region of interest is close to the zone boundary at \(k = \sqrt{3\pi/a} \), the quantum number \(n\) is a large number. This is inconvenient. Instead, we wish to measure \(k\) from the zone boundary; we call this \(k'\). The quantization condition can be rewritten in terms of \(k'\) and a new quantum number \(\nu = N - n\) as shown.

The quantum number \(\nu\) assumes small values 1, 2, 3, ... near the band edge. Specifically, \(\nu = 1\) corresponds to the quantum well state closest to the band edge. As the film thickness changes, this \(\nu = 1\) peak appears to move smoothly. If the quantum number \(n\) is used, instead, to label the same state, it would change for different film thicknesses because \(n = N - \nu\). Specifically, \(n = 29, 23, 18, 14, 11, \) and 9 for the cases shown in the figure for the same \(\nu = 1\) peak. This labeling would be inconvenient. Note that there is an effective sign reversal for the phase shift as we make the transformation from \(n\) to \(\nu\). Sometimes in the literature, the quantum number \(\nu\) is labeled as \(n\). So, please be careful.

The film thickness \(N\) must be an integer. While the \(\nu = 1\) peak in the data appears to move smoothly as a function of \(N\), the movement should be discrete because \(N\) is quantized. One could instead use \(n\) to label the peaks and "connect" the peaks with the same \(n\) for different film thicknesses. The results would not be particularly appealing for Ag on Au. Labeling in terms of \(n\) is best for states near the zone center. However, how one "connects the dots" can be a matter of personal choice. For Pb(111) films, both labeling schemes are fine choices, as the region of interest is close to midway between the zone center and zone boundary. As one can imagine, there can be yet other schemes to label the states.
Figure 39 shows the calculated probability densities for the quantum well states in a 24 ML Ag film on Au and the same film imbedded in Au. The calculation is based on a simple two-band model (lowest order pseudopotential model). Recall the particle-in-a-box model where the wave functions are sinusoidal. The wave functions here look more complex.

For the particle-in-a-box model, the probability density for $n = 23$ ($\nu = 1$ and $N = 24$) should have 23 peaks with identical height. A counting of the Au/Ag/Au case shows 23 peaks within the film and a few small peaks in the tails inside the Au. The peaks are modulated by an envelope function that looks like the $n = 1$ probability density for the particle-in-a-box case. An examination of the calculated results yields the physical interpretation for the quantum number $\nu$: it is the number of antinodes associated with the envelope function.

The envelope function arises from the crystal potential. It can be viewed as a beating pattern involving the two plane waves in the two-band model with the wave vectors $k$ and $k - G$, where $G$ is the primitive reciprocal lattice vector along [111].

Let us return to the case of Ag films grown on Si(111) (Fig. 40). Si has a gap, but all of the quantum well peaks (not including the surface state peak near the Fermi level) are below the gap, and so all of them are actually quantum well resonances. There is a large mismatch between the electronic structure of Ag and Si, which leads to substantial electron reflection at the Ag-Si boundary.
The examples thus far show quantum well states (or resonances) that seem to evolve smoothly as a function of film thickness $D$. However, the film thickness is quantized ($D = Nt$, where $t$ is the monolayer thickness). The quantum well peaks must show discrete behavior as the film thickness changes one monolayer at a time.

Early experiments did not reveal this discrete peak behavior. The main reason is that the films were not smooth as shown in Fig. 41. Multiple thicknesses give rise to multiple peak positions that are not necessarily resolved. Small domain sizes can lead to peak broadening. Quantum well peaks for such films are broadened, with the peak positions correspond to the average film thickness.

Ideally, one would like to work with atomically uniform films with exactly known thicknesses in terms of the atomic layer. The first successful experiment was performed on Ag(100) films grown on Fe(100). The Fe(100) substrate was a highly perfect whisker sample.

This set of normal emission spectra in Fig. 42 illustrates the discrete atomic layer behavior for Ag(100) films grown on Fe(100). The film was deposited onto Fe(100) at about 100 K, and then it was annealed to near room temperature.

The spectrum for the 38 ML Ag film shows 5 sharp quantum well peaks. The spectrum for the 39 ML Ag film also shows sharp quantum well peaks, but at somewhat different positions. The peak just below the Fermi level at 38 ML has moved to a position above the Fermi level at 39 ML, and therefore it is not seen. At a coverage of 38.5 ML, two sets of peaks are seen, one set corresponds to 38 ML, and the other corresponds to 39 ML. The interpretation is straightforward: the film has domains of thicknesses 38 and 39 ML, and the spectrum is a mixture. The two sets of peaks are resolved. Note that for the 38 ML
film, we detect no traces for the 39 ML peaks. In fact, we also detect no traces for the 37 ML peaks. So, the 38 ML film has a uniform thickness of 38 ML throughout the entire surface. The film is atomically uniform.

Such uniform films can be prepared by deposition at low temperatures (100 K and below) followed by annealing to near room temperature. To increase the film thickness, additional deposition is made at low temperatures and then the film is annealed. The resulting thicker film remains atomically uniform as long as the total deposition corresponds to an integer number of atomic layers. Deposition at room temperature or higher results in non-uniform films with multiple thicknesses.

For the 38 ML film, how do we know that the thickness is 38 (not 39 or 37) ML? We need a method to do an absolute calibration. This was done by atomic layer counting (see next slide).

Fig. 43

The normal emission spectra on the left in Fig. 43 were taken from samples prepared by adding Ag in small incremental amounts. The discrete layer behavior allows us to calibrate the film thickness in terms of the exact number of atomic layers. As the deposition increases, the 1 ML peak becomes fully developed first. It then fades away and simultaneously a 2 ML peak emerges. The 1 ML peak disappears completely when the 2 ML peak becomes fully developed. Upon further deposition, the 2 ML peak diminishes and simultaneously a 3 ML peak emerges, etc. The spectra shown are for the films with integer monolayer coverages. The results allow us to perform an absolute calibration of the deposition. Also, the measured peak positions permit an extrapolation to determine the peak positions at higher thicknesses. The figure on the right shows additional spectra to higher thicknesses. Quantum well states are seen for thicknesses well over 100 ML. Since these states arise from interference involving the two boundaries, the results suggest a very long quasiparticle coherence length.

Note that the photoelectron escape depth is just a few Angstroms. Yet we can observe quantum well peaks characteristic of interference involving the surface and the interface that are separated by a distance much greater than the escape depth. In this sense, photoemission has a long probing depth of the order of the quasiparticle coherence length. Indirect or surface transitions caused by a non-zero divergence A is the mechanism of photoemission from quantum well states in this case.
It is interesting to note that digital data processing is standard these days. Some of the data presented in the lectures were taken and processed before the digital era. The spectra shown in Fig. 44 for the quantum well states in Ag(100) films on Fe(100) were recorded digitally, but out of old habit we also recorded the data in analog form on paper using a chart recorder.

We see very sharp quantum well peaks in Ag films on Fe(100), suggesting that the Ag-Fe boundary is highly reflective, or that the Ag electrons are well confined. The relevant band structures of Ag and Fe along [100] are shown in Fig. 45. The Ag band structure is characterized by d bands between approximately -4 and -7 eV. The bottom of the sp band is at about -8 eV. The portion of the sp band above the d bands is responsible for the quantum well states. The Fe band structure is spin polarized. The minority band structure, shown in the figure, looks like a stretched version of the Ag band structure. The sp band begins at about -8 eV. The d bands are approximately between -3 and +2 eV. This region is called a hybridization gap for the sp states. The Ag sp states do not couple (well) to the d states in Fe because of the difference in symmetry. Thus, the Ag sp electrons with the minority spin
orientation are fairly well confined in this energy range by the hybridization gap. The majority spin electrons are less well confined. Experimentally, it has been shown that the quantum well states in very thin Ag films on Fe are polarized in the minority spin direction.

Quantum well spectroscopy is very useful for absolute band mapping, as illustrated by the example shown in Fig. 46. Since the total boundary phase shift $\Phi$ is generally unknown, it is not possible to determine $k$ for a given $n$ based on the Bohr Sommerfeld quantization condition using just one spectrum.

The normal emission spectra are taken from atomically uniform films of Ag on Fe. Two of the quantum well peaks for $N = 28$, with quantum number $n$ and $n' = n + 1$, are indicated by circles. As the film thickness increases, the $n'$ state at higher binding energy moves toward lower binding energy. Eventually, at $N' = 71$, its position coincides with the $n$ state at $N = 28$. The quantization conditions for the two cases $(N', n')$ and $(N, n)$ are shown; they involve the same energy and same $k$ at the point of coincidence. The total boundary phase shift $\Phi$ is also the same because it is only a function of energy. Solving this pair of equations yields $k$ and $\Phi$ at the particular energy $E$. This yields an absolute measure of a point for the dispersion relation $E(k)$. The procedure can be repeated for other pairs of peaks to get the $E(k)$ relations at other energies. Exact coincidence of peaks is relatively rare, but one
could easily use an interpolation scheme to find the energy positions for each peak at non-integer thicknesses and still perform the same analysis. Thus, it is straightforward to deduce the band structure over the energy range where quantum well peaks are observed, as long as the absolute film thicknesses are known and the data cover a number of film thicknesses. In practice, one can employ suitable functions with a few adjustable parameters to model the band dispersion $k(E)$ and the phase shift $\Phi(E)$ and perform a global fit to all of the observed quantum well peak positions.

Such an analysis has been carried out for Ag/Fe as shown in Fig. 47. The "structure plot" shows the experimental quantum well peak positions (circles) at various thicknesses. The curves are calculated results based on the fit. For the calculation, one is free to use non-integer film thicknesses. The band structure function is taken from a two-band model, and the phase shift is assumed to be a smooth low order polynomial.

The differences between the fits and the data are shown in the lower panel. The randomness indicates noise in the data. However, systematic deviations, though small, are seen for $N = 1, 2$, and maybe 3. This can be explained by inaccuracies in the Bohr-Sommerfeld condition. This condition assumes that there are distinct phase shifts at the two boundaries. The physical boundaries are actually somewhat blurred for electrons that propagate quantum mechanically. In other words, the assumed Bloch form of the electron waves might not be exactly applicable in regions very close to the boundaries. Significant deviation can happen within a length of the order of the Debye screening length, or about the atomic dimension. For films as thin as $N = 1, 2,$ and 3, the tails of the two boundary potential variations can overlap, causing errors in the above analysis. Our results indicate that the deviation even at $N = 1$ is not that large, just about 0.1 eV.

Based on the model fitting results, the "energy level diagram" or structure plot for Ag(100) films on Fe(100) along the surface normal direction is shown in Fig. 48. The curves connect the energy levels of the same quantum numbers for different film thicknesses. Again, film thicknesses are quantized. The continuous curves are just a guide to the eye. However, if the films are rough, the continuous curves may represent the average quantum well peak positions.
Unlike the direct transition peaks from bulk crystals, which have asymmetric lineshapes, quantum well peaks have symmetric lineshapes. What is the meaning of the peak width? On the left in Fig. 49 is a normal emission spectrum from an optimally prepared 29 ML of Ag on Fe. After adding 0.05 ML of Ag on top of the surface without annealing, the quantum well peaks become substantially broader. This result shows that quantum well peak widths can depend critically on the surface condition, or film quality in general.

For the best films, we can talk about intrinsic broadening effects. On the right, the peak widths are shown for a couple of spectra. We can conclude from a survey of a large data set that: (1) the peak widths become smaller toward the Fermi level for a given thickness. This can be attributed to a reduced electron-electron scattering rate due to a reduced phase space for scattering; (2) the peak width is smaller for thicker films at the same energy. This can be attributed to a reduction of boundary scattering. A more detailed explanation follows.

\[
\psi_1 \propto 1 + r_1 r_2^* e^{i(2kN\Phi + \phi_1)} + \cdots
\]

\[
= \frac{1}{1 - R e^{i(2kN\Phi + \phi_1)} e^{-Nl/\lambda}}
\]

R = \eta r_2; \quad \Phi = \phi_1 + \phi_2

\[
I \propto \frac{1}{1 + \frac{4f^2}{\pi^2} \sin^2 \left( kN \Phi + \frac{\pi}{2} \right)}
\]

f = \frac{\pi \sqrt{Re^{-Nl/2\lambda}}}{1 - Re^{-Nl/\lambda}} = \text{finesse}

Peaks at \(2kN\Phi + \Phi = 2n\pi\) Bohr-Sommerfeld quantization rule

\[\lambda = \text{mean free path (e-e scattering, phonon scattering, impurity, ...)}\]

Paggel, Miller, & Chiang, Science 283, 1709 (1999)

Fig. 50

The photoemission final state is a time-reversed LEED state, as discussed earlier. Here, we will consider the time reversed situation to describe the wave function (Fig. 50). Upon time reversal, the photoelectron travels from the detector to the sample surface, where it makes a transition to the initial state and emits a photon. The electron in the initial state travels toward the inside of the sample, encounters the interface, and splits into a transmitted wave and a reflected wave. The reflected wave from the interface travels to the surface and gets reflected backward, etc. Inside the film, the electron travels back and forth. The situation is just like a Fabry-Perot interferometer. Quantum well states are formed when the multiple reflections result in constructive interference.

Quantum mechanically, the wave function inside the film is just a coherent sum from the multiply reflected waves, where \(r_1 \exp(i\phi_1)\) and \(r_2 \exp(i\phi_2)\) are the complex reflection coefficients at the surface and interface, respectively. The electron can suffer scattering while it travels through the film, and this is modeled by a mean free path \(\lambda\). The sum is just a geometric series and can be evaluated easily. The photoemission intensity is proportional to the absolute square of the wave function. The final result is just the Airy function that describes the Fabry-Perot response of a lossy medium. A series of resonances (peaks) are located at positions specified by the Bohr-Sommerfeld quantization condition (the intensity is a maximum when the sine function in the denominator vanishes). Thus, this boundary condition is not an "ansatz": rather, it follows from wave mechanics. Note
that the wave vector $k$ here is the Bloch wave vector. It is related to the electron energy by the band structure.

The peak width is determined by the quantity $f = \text{finesse}$. It is the ratio of peak separation and peak width. A higher finesse means a better interferometer and a narrower peak width. It depends on $R = r_1r_2$, which is related to the boundary reflectivities, and the mean free path $\lambda$. As the electron in the initial state undergoes multiple bounces between the two boundaries to form a standing wave, its amplitude suffers losses in the film due to a finite mean free path, and at the boundaries due to less than unity reflectivities. The larger the loss, the wider the peak width becomes.

The mean free path is related to the quasiparticle lifetime and the group velocity. The above analysis shows that the measured quantum well peak widths are generally wider than the quasiparticle lifetime widths; the additional contribution comes from boundary scattering. The two contributions can be separately determined if finesse measurements are available at two (or more) different film thicknesses.

The Airy function is used to fit the quantum well spectra of Ag on Fe for many different thicknesses. The fit incorporates smooth low order polynomials to describe the cross section (or matrix element) variation, background emission, etc. The results are summarized in Fig. 52. The band structure determined is the most accurate thus far: the Fermi level crossing is likely more accurate than that determined from the de Haas-van Alphen method. The combined boundary reflectivity is close to but less than unity, as expected. The quasiparticle lifetime width has a constant term and a quadratic term. The constant term can be attributed to phonon and defect scattering. The quadratic term can be attributed to electron-electron scattering. The combined boundary phase shift shows substantial variation over the region of interest.
Note that the quantum well states in Ag/Fe correspond to the minority spin polarization. The majority spin electrons are not well confined; presumably they contribute to the background.

The analysis is one-dimensional because the measurement is carried out with a normal emission geometry.

What about thermal effects? As the sample temperature rises, the quantum well peaks become broader as shown in Fig. 53. The increased peak width suggests a shorter lifetime or an increased scattering rate. Electron-electron scattering is largely temperature independent. The increased scattering rate here is caused by phonon scattering. The phonon population rises for increasing temperature, and the phonon scattering rate is directly proportional to the phonon population.

The electron phonon scattering rate is additionally determined by the electron-phonon coupling strength (or matrix element). If the coupling is exactly zero, the quantum well peak width would be independent of temperature. It is easy to see that the rate at which the quasiparticle lifetime width increases as a function of temperature (in the high temperature limit) is related to the electron-phonon coupling strength. This quantity is of fundamental interest and is relevant to superconductivity. BCS superconductivity depends on Cooper pair formation, which needs a large electron-phonon coupling.

Quantum well spectroscopy yields a very accurate band structure because it is an interferometric measurement. For Ag films on Fe(100), the Fermi wave vector (or the place in k space where the sp band crosses the Fermi level) changes very slightly as a function of temperature, as shown in Fig. 54.

There is a slight complication in the analysis. As the temperature changes, the lattice constant of the Ag film changes correspondingly because of thermal expansion. The change in film thickness (or the width of the quantum well) must be accounted for.
The widths of quantum well peaks depend on the boundary reflectivities and the quasiparticle lifetime. One can extract the quasiparticle lifetime from the data as discussed earlier. The lifetime width has three contributions as shown in Fig. 55: defect scattering, which is a constant, phonon scattering, which depends on temperature, and electron-electron scattering, which depends on the square of the binding energy relative to the Fermi level. The phonon contribution involves a parameter $\lambda$, the so-called electron-phonon mass enhancement parameter (or just the electron-phonon coupling parameter, for short). The formula for the total width shown assumes that we are away from the Fermi level by at least ~ the Debye energy. At energies very close to the Fermi level, the formula is more complex as there are other issues related to the phase space for scattering. This formula was used to analyze the temperature-dependent data. The electron-electron scattering part is subtracted away, and the figure shows the phonon and defect scattering contributions together and separately. The defect contribution, 8 meV, is fairly small.

The mass enhancement parameter $\lambda$ is 0.29 for large film thicknesses from this analysis. A survey of the periodic table shows that most BCS superconductors have $\lambda$ over about 0.3, and elements with $\lambda$ less than 0.3 are generally not superconductors (or have unmeasurably low superconducting transition temperatures). A strong electron-phonon coupling is essential for Cooper pair formation. The value of 0.29 for Ag is close to this threshold value. Naturally, one wonders if $\lambda$ has a thickness dependence. If $\lambda$ is larger at smaller film thicknesses, there is a

**Fig. 55**

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**Quasiparticle Lifetime Width**

(no boundary contributions)

$$w(E,T) = w_0 + w_1(T) + w_2 E^2 \quad (\text{for } E > 50 \text{ meV})$$

$$w_0 = 8 \text{ meV (defect)}$$

$$w_1(T) = 2\pi \int_0^{\omega_D} \left[ 1 - f(\omega - \omega') + 2b(\omega') + f(\omega + \omega') \right] d\omega'$$

$$w_2 = 256 \text{ meV}/eV^2$$

(phonon scattering)

$$\lambda (\text{mass enhancement parameter}) \text{ at large thicknesses} = 0.29 \ (2 \times \text{theory})$$

Ag almost superconducting? (BCS threshold = 0.3)
possibility for novel or enhanced superconducting behavior. However, since Fe is ferromagnetic, which tends to suppress superconductivity, Ag/Fe is probably not a good candidate for this quest.

So far, the discussion has focused on the sp band. Shown in Fig. 56 is the band structure of Ag again. Can the d bands also support quantum well states? This question arises because the d states are more localized than the sp states. One anticipated problem is that these bands have very little dispersion: the quantum well states would be very closely spaced and might not be resolvable.

Figure 57 shows normal emission spectra in the d band region for different Ag film thicknesses on Fe(100). Evidently, quantum well states do exist for the d bands. A number of quantum well peaks are seen, but many of them are not resolved. The band structure and the phase shift from a detailed analysis are shown.

Details near the top of the d bands are shown in Fig. 58. The peaks at lower binding energies are sharper. The topmost peak is the sharpest. Its decay by electron-electron scattering is limited to Auger processes involving the sp band. Because of the difference in symmetry between sp and d states, the Auger coupling is weak, and so the peak width is narrow. The deeper d states are wider because they can decay by the more efficient Auger processes involving other d states.
A detailed analysis has been performed for the topmost $d$ quantum well state. The peak width depends on both the combined reflectivity and the quasiparticle lifetime width. With measurements over a number of different thicknesses, the two contributions can be separated out. The results are shown in Fig. 59. The intrinsic lifetime width of 13 meV is the smallest ever reported for any state at such a large binding energy.

Presented in Fig. 60 is a case that well illustrates the concept of quantum-well resonances as incompletely confined quantum well states. The system consists of a Ag(111) substrate, a $x$-ML Au barrier ($x = 0, 2,$ and 3), and an over layer of 15 ML Ag as a quantum well. Because the Au barrier layer is very thin, the sp electrons in the Ag...
overlayer, even with energies within the Au gap, are not completely confined because of quantum tunneling; the exponential tail of the decaying wave can penetrate the barrier and reach the substrate. For energies outside the Au gap, the Ag electrons are partially reflected at the boundary. In either case, the Ag film can be regarded as a "leaky" quantum well.

With \( x = 0 \), the spectrum is just that for single crystal Ag(111). With \( x = 2 \) or 3, the indirect transition region breaks up into quantum-well states (actually, resonances) as indicated. Also shown are calculated spectra for comparison. The agreement is fairly good, although the peaks seem to be wider experimentally possibly due to sample imperfections. The calculation uses the two band model for the band structure.

Shown in Fig. 60 on the right are probability densities of the initial states at a few energies for \( x = 2 \). Note that the surface state is truly confined near the surface. The other states are not. At energies below the Ag band edge, the system has a continuum of states. At 0.4 and 0.9 eV (away from quantum well resonances), the wave functions assume the bulk form in the Ag substrate, and have low amplitudes in the Ag film. At 0.6 and 1.23 eV, corresponding to the \( \nu = 1 \) and 2 resonances, respectively, the wave functions are again bulklike in the substrate, but have much higher amplitudes in the film. In each case, the higher amplitude accounts for the higher photoemission intensity at the resonance peak. The \( \nu = 1 \) and 2 resonances correspond to 1 and 2 antinodes, respectively, for the envelope function in the Ag film. The situation is very similar to Ag films on a Au substrate.

To summarize, quantum well states are discrete states associated with full confinement. The spectral function of the system consists of a set of delta functions (assuming the electrons do not decay). Leaky quantum well systems have a continuum of states, but the wave functions can pile up in the quantum well region around resonances. The spectral function is a continuous function of energy, with a series of broadened resonance peaks. The distinction between the two cases is not necessarily clear-cut when scattering and lifetime effects are included for quantum well states.