Quantum modulation of the Kondo resonance of Co adatoms on Cu/Co/Cu(100)

Takashi Uchihashi,1,2 Jianwei Zhang,1 Jörg Kröger,1 and Richard Berndt1
1Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany
2Nano System Functionality Center, National Institute for Materials Science, Tsukuba 305-0044, Japan
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Low-temperature scanning tunneling spectroscopy reveals that the Kondo temperature \( T_K \) of Co atoms adsorbed on Cu/Co/Cu(100) multilayers varies between 60 K and 134 K as the Cu film thickness decreases from 20 to 5 atomic layers. The observed change of \( T_K \) is attributed to a variation of the density of states at the Fermi level \( \rho_F \) induced by quantum well states confined to the Cu film. A model calculation based on the quantum oscillations of \( \rho_F \) at the belly and the neck of the Cu Fermi surface reproduces most of the features in the measured variation of \( T_K \).

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Magnetic atoms interacting with their environment are fundamentally important in extensive fields of modern physics. Among all, the Kondo effect, a representative phenomenon resulting from the exchange interaction of a local spin with surrounding conduction electrons, is observed below a characteristic Kondo temperature \( T_K \). One of its hallmarks is the Kondo resonance whose width is given by \( k_B T_K \) (\( k_B \): Boltzmann’s constant). The Kondo resonance may be directly investigated using low-temperature scanning tunneling microscopy (STM) or various quantum dots. Furthermore, artificial modification of the Kondo effect was investigated using atom manipulation and controlled tip contact. More recently, a molecular Kondo effect has been investigated. Apart from the Kondo effect, the recent advancement of the spintronics has raised a strong interest in spin manipulation and in tailoring exchange interaction at atomic scale. The observation of spin-related phenomena using low-temperature STM and their control with artificial nanostructures are crucial for realizing such promises.

Here we use a model system for tuning the single-adatom Kondo temperature by means of variations of the local density of states at the Fermi level. In particular, single Co atoms are adsorbed on multilayers of Cu and Co grown on a Cu(100) surface and modifications of the Kondo resonance are measured as a function of the Cu layer thickness. Scanning tunneling spectroscopy is used to identify quantum well (QW) states of the Cu film. The absolute thickness of Cu overlayers, \( d_{\text{Cu}} \), is locally determined from characteristic QW state energies. The Kondo temperature determined from spectra of the differential conductance \( (dI/dV) \) taken on single Co adatoms varies between 60 K and 134 K with decreasing Cu coverage from 20 to 5 atomic layers. Much of this variation is reproduced by a model calculation based on the quantum oscillations at the belly and the neck of the Cu Fermi surface. The phases of these oscillations are found to deviate from a theoretical prediction for Cu/Co/Cu(100) multilayers, suggesting the effect of Co adatoms on the phase shift at the Cu/vacuum interface.

The experiments were performed with a home-built low temperature STM operated at 7 K and in ultra-high vacuum with a base pressure of \( 10^{-9} \) Pa. Samples and W tips were prepared by annealing and argon ion bombardment. Crystalline order was checked by low-energy electron diffraction (LEED) while preliminary estimates of Co and Cu film thicknesses were performed by Auger electron spectroscopy (AES). Spectra of \( dI/dV \) were acquired by standard lock-in detection. The clean Cu(100) surface was covered at room temperature (RT) with 10 ML of Co using an electron beam evaporator and an evaporant of 99.99% purity. We define a monolayer (ML) as one Co atom per Cu atom. Subsequently, Cu was deposited at RT on the Co surface from a copper wire of 99.995% purity wrapped around a tungsten filament. High deposition rates of \( \approx 6 \) ML min\(^{-1} \) were necessary to suppress heating from the filament and concomitant intermixing of Cu and Co. Co atoms were deposited on the cold surface by electron beam evaporation.

We adopted a Cu/Co/Cu(100) system as a substrate for tuning the Kondo effect because extensive studies on this multilayer system are available. An excellent lattice matching enables epitaxial growth of a face-centered cubic Co(100) layer on Cu(100), rather than a bulk-like hexagonal close-packed Co layer, and a subsequent epitaxial growth of Cu(100) on Co(100) (Fig. 1(a)). Figure 1(b) presents a constant-current STM image of Cu(100) with a Co coverage of 10 ML which reveals layer-by-layer epitaxial growth of Co. A subsequently deposited Cu layer exhibits pyramid-shaped islands with a lateral size of \( \approx 20 \) nm (Fig. 1(c)). The resulting layered surface is an ideal platform for acquiring spectra at a variety of Cu layer thicknesses without changing the image area. Figure 1(d) is a typical STM image of single Co adatoms on a Cu/Co/Cu(100) multilayer. Although the density of adatoms is rather high (typically 0.2 atoms/\( \mu \)m\(^2\)), the Kondo effect remains intact as far as single adatoms appear separated from each other in an STM image.

While a nominal thickness of a Cu overlayer can be estimated from the deposited amount of Cu, its local thickness varies substantially. We determined the local thickness from the energies of QW states of the Cu overlayer. Since the Cu Fermi surface is lo-
cated near the Brillouin zone boundary, the wave function of an electronic state near the Fermi level \( E_F \) with wave number of \( k \) is modulated by an envelope function with \( k_{\text{env}} = k_{\text{BZ}} - k \), where \( k_{\text{BZ}} \) is the wave number at the Brillouin zone boundary. QW states occur when electrons are reflected at the two interfaces and interfere constructively. For an electron state with \( k_{\text{env}} \) and energy \( E \), this condition is satisfied when the layer thickness \( d_n \) is given by:

\[
d_n = \left[ n - 1 + \frac{\Phi(E)}{2\pi} \right] \frac{k_{\text{BZ}}}{k_{\text{env}}},
\]

where \( \Phi(E) \) is the total phase shift caused by the reflections and \( n \) is an integer. For \( E \), \( k_{\text{env}} \) is determined by the energy dispersion of the relevant \( sp \) band (see Fig. 2(b)). Because the dispersion of the Cu \( sp \) band is precisely known near \( E_F \), the thickness of the Cu layer can be determined from the energies of the QW states.

Figure 2(a) shows a series of \( dI/dV \) spectra taken on different surfaces of Cu/Co/Cu(100) multilayers. Clear peaks are visible within the range of 0 to 2 V indicating the presence of QW states in this energy range. The local thickness of the Cu overlayer was determined by comparison of the experimentally obtained peak energies with calculations. The energy dispersion of the Cu \( sp \) band along the [100] direction near \( E_F \) can be described by the two-band nearly-free electron model:

\[
k_{\text{env}} = \sqrt{1 + \frac{E + E_F}{G} - \sqrt{\frac{4(E + E_F)}{G} + \left(\frac{U}{G}\right)^2}},
\]

where \( E \) is the QW state energy measured relative to the Fermi level, \( G = h^2 k_{\text{BZ}}^2 / 2m^* \) (\( m^* \) is the effective mass of the electron), \( U \) is half the energy gap at the Brillouin zone boundary. Following the analysis of QW states observed with inverse photoemission spectroscopy (IPES) by Ortega et al., we insert \( E_F = 7.39 \text{ eV}, G = 12.27 \text{ eV}, \) and \( U = 3.08 \text{ eV} \) into Eq. (2) and a linear phase-energy relation \( \Phi(E) = 0.35 \pi eV \times E \) into Eq. (1).

Figure 2(c) displays the calculated thickness of a Cu overlayer as a function of QW state energies (solid lines) together with IPES data (squares) An absolute thickness was determined for each spectrum in Fig. 2(a) by referring to these theoretical curves (see the thicknesses labeled beside the graph). Note that the relative thicknesses within a group (6 – 8 ML, 9 – 13 ML, 14 – 20 ML) were determined by a simultaneously observed surface topography. A schematic dispersion curve of the Cu \( sp \) band along the [100] direction (T-X). (c) Peak energies of \( dI/dV \) spectra in Fig. 2(a) as a function of Cu overlayer thickness \( d_{\text{Cu}} \) (dots). Calculated energies of QW states (solid lines) and IPES data (squares) are included.
experiment and the theory shows the validity of the present analysis. The thickness determination error is estimated to ±1 ML.

After determining $d_{Cu}$, we measured $dI/dV$ spectra on single Co atoms on Cu/Co/Cu(100) multilayers. Before performing spectroscopy, the STM tip was shaped by touching a Cu surface area until Co adatoms appeared circular and $dI/dV$ spectra of a bare Cu surface became featureless around zero sample voltage. For analysis of the Kondo resonance, remaining artifacts due to the tip electronic structure were removed by dividing spectra of single Co atoms by an averaged spectrum of the clean Cu surface on the same terrace. The top and middle graphs in Fig. 3(a) are representative spectra for $d_{Cu} = 14$ ML and $d_{Cu} = 11$ ML, respectively (solid lines). As a reference, a similar measurement on a pure Cu(100) substrate is shown at the bottom of Fig. 3(a). The characteristic line shapes asymmetric around $V = 0$ indicate the Kondo resonance on these Co adatoms. In $dI/dV$ spectra the Kondo resonance generally appears as an asymmetric line shape or even as a dip due to the Fano effect. This assignment was further confirmed by disappearance of the characteristic line shape when the tip was moved off the adatom center only by 0.5 nm.

To quantitatively analyze the $dI/dV$ spectra, we fit the following Fano line shape to the data:

$$\frac{dI}{dV} = a \frac{(q + \epsilon)^2}{1 + e^2} + b + cV$$

with $\epsilon = (eV - \epsilon_K)/k_B T_K$. Here, $q$ is the asymmetry parameter of the Fano theory, $\epsilon_K$ a resonance shift from the Fermi level, and $a$ the amplitude of the resonance. A linear voltage dependence $b + cV$ was added to account for the contribution of conduction electron states not involved in the Kondo resonance. Equation (3) was fitted to the above three spectra, with the results shown in the same graphs as dashed lines. The Kondo temperatures 67 K and 139 K were obtained for $d_{Cu} = 14$ ML and $d_{Cu} = 11$ ML, respectively, which significantly deviate from $T_K = 90$ K for pure Cu (100).

We performed analogous experiments for Cu/Co/Cu(100) multilayers with Cu coverages ranging between 5 and 20 ML. The total number of samples and of spectra analyzed is 10 and 156, respectively. The Fano line shape of Eq. (3) was fitted to all individual spectra to obtain $T_K$ as described above. The whole data set was divided into groups according to $d_{Cu}$, and the average and the standard error of $T_K$ were calculated for each $d_{Cu}$. Figure 3(b) displays the averaged $T_K$ as a function of $d_{Cu}$ (circles connected by dashed line) with half the error bar representing the standard error. Measurements on Co adatoms on pure Cu(100) were also repeated to obtain an averaged $T_K = (94 \pm 5)$ K $\equiv T_{K,0}$, which is consistent with previous reports. $T_{K,0}$ is shown as a horizontal dashed line in Fig. 3(b) as a reference. Clearly, the Kondo temperature $T_K$ is modulated as a function of $d_{Cu}$. This $T_K$ modulation is attributed to variations in the density of states at the Fermi level, $\rho_F$, caused by QW states of the Cu overlayer. The Kondo temperature depends on $\rho_F$ through the following relation:

$$T_K = T_0 \exp \left( -\frac{1}{2\rho_F J_{sd}} \right)$$

where $T_0$ is a prefactor and $J_{sd}$ the $s$-$d$ exchange coupling constant. This interpretation is plausible since we have proved the presence of QW states and their evolution with $d_{Cu}$ in our samples. For a Co adatom on pure Cu(100), inserting $\rho_F = 0.11$ eV$^{-1}$ and $J_{sd} = 1.0$ eV gives $T_{K,0} = 9800$ K. $T_K$ is sensitive to a small variation in $\rho_F$ under this condition. Since the quantum confinement in the Cu/Co/Cu(100) multilayer is weak, $\rho_F$ at the surface of the Cu overlayer is expressed by

$$\rho_F = \rho_{F,0} + \sum_{i=b, n} A_i \frac{d_{Cu}}{\Lambda_i} \cos \left( \frac{2\pi d_{Cu}}{\Lambda_i} + \Phi_i \right)$$

FIG. 3: (Color online) (a) $dI/dV$ spectra measured on Co adatoms on Cu/Co/Cu(100) multilayers. Top: 14 ML Cu. Middle: 11 ML Cu. Bottom: pure Cu(100). Spectra are offset for clarity. Dashed lines indicate fits to experimental data according to Eq. (3). (b) Averaged Kondo temperature $T_K$ of Co adatoms on Cu/Co/Cu(100) multilayers as a function of Cu overlayer thickness $d_{Cu}$ (circles connected by dashed line). Half the error bar represents the standard error of $T_K$ calculated for each $d_{Cu}$. Calculated $T_K$ is plotted as a solid line. The fit parameters used are $A_b = 0.046$ eV$^{-1}$ ML, $\Phi_b = 0.26\pi$, $A_n = 0.011$ eV$^{-1}$ ML, $\Phi_n = -0.03\pi$. Averaged $T_K = 94$ K for Co adatoms on pure Cu(100) surfaces appears as a dotted line.
Here, $A_i$, $\Lambda_i$, and $\Phi_i$ are the amplitudes, spatial periodicities, and phases of the quantum oscillations at the belly ($i = b$) and the neck ($i = n$) of the Cu Fermi surface. While the periodicities have been precisely determined ($\Lambda_b = 5.88$ ML and $\Lambda_n = 2.67$ ML) [10,21], the amplitudes and the phases are less established. We therefore fit $T_K$ calculated with Eqs. [1] and [2] to the experimental data by keeping $\Lambda_i$ fixed and leaving $A_i$ and $\Phi_i$ as free parameters. The result is plotted in Fig. 3(b) (solid line) with $A_b = 0.046$ eV$^{-1}$ ML, $\Phi_b = 0.26\pi$, $A_n = 0.011$ eV$^{-1}$ ML, and $\Phi_n = -0.03\pi$. The fit reproduces most of the aspects of the data; local maxima at $\approx 5\pi$, $\approx 7\pi$, and $\approx 14\pi$ are described as well as local minima at $\approx 7\pi$ and $\approx 8\pi$. Note that the phases determined here deviate from a theoretical prediction of $\Phi_b = 0.12\pi$ and $\Phi_n = 0.69\pi$ for Cu/Co/Cu(100) multilayer [22] by $0.14\pi$ and $-0.72\pi$, respectively. This may be attributed to additional phase shifts due to the very presence of the Co adatoms. Assuming that electron wavefunctions penetrate from the Cu surface to the vacuum side by a Co atomic height, this will result in an additional phase shift of $2\pi/\Lambda_b = 0.34\pi$ and $2\pi/\Lambda_n = 0.75\pi$ for $\Phi_b$ and $\Phi_n$, respectively. We thus call for theoretical investigations on the effect of Co adatoms on the phase shift of the quantum oscillations.

Finally, we remark that the exchange interaction between a Co adatom and the Co layer through Cu, $J_{ex}$, is too weak to account for the observed variations in $T_{K,0}$. According to an $ab$ initio calculation by Brovko et al. [12], $J_{ex}$ is 1.5 meV for $d_{Cu} = 5$ ML and rapidly decreases with increasing $d_{Cu}$. This is small enough considering the energy scale of the Kondo effect $k_BT_{K,0} = 8.1$ meV observed here. However, $J_{ex}$ was found to become comparable to or even much larger than $k_BT_{K,0}$ for $d_{Cu} \leq 4$ ML. This should result in suppression and/or splitting of the Kondo resonance [20,21]. Furthermore, they predicted that the exchange interaction between two Co atoms adsorbed on a Cu/Co/Cu(100) multilayer can be tailored by changing the Cu overlayer thickness. Our demonstration of tuning the Kondo effect by means of the same multilayer system promises experimental feasibility of such forthcoming studies.

In summary, we observed a modulation of the Kondo temperature of single Co atoms adsorbed on Cu/Co/Cu(100) multilayers depending on the Cu layer thickness. A model based on local density of states oscillations at the Fermi level owing to confined QW states reproduces most of the observed variations. The analysis on the $T_K$ modulation suggests unexpected phases of the quantum oscillations in the Cu overlayer, which requires further experimental and theoretical efforts.

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[* Electronic address: UCHIHASHI.Takashi@nims.go.jp*]

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We find that the Fano factor $q$ varies significantly on Cu/Co/Cu(100) multilayers, reflecting changes in the spectrum shape. This may be caused by quantum interference in the Cu overlayer.

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