

Kondo Effect in Self-Assembled Manganese Phthalocyanine Monolayer on Pb Islands *

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(Received 6 April 2010)

The Kondo effect in two-dimensional manganese phthalocyanine (MnPc) self-assembled monolayer films on Pb(111) islands is studied by low-temperature scanning tunneling microscopy. Variation of the Kondo temperature from 50 K to 300 K at different molecule adsorption sites is revealed. It is shown that the variation is mainly due to the change in the width of d orbital, rather than the shift of its energy. The two-dimensional dI/dV mapping reveals the periodic modulation of the Kondo resonance in the self-assembled MnPc monolayer.

PACS: 72.15.Qm, 68.37.Ef, 68.55.-a

DOI: 10.1088/0256-307X/27/8/087202

The Kondo effect originates from the interaction between the local spin of an impurity/adsorbate and the conduction electrons in a host metal.^[1] When the temperature is lower than the Kondo temperature, the local spin will be fully screened by the conduction electrons and a Kondo resonance peak will appear at the Fermi level. The study of the Kondo effect has been pushed down to the single atomic level since the development of low temperature scanning tunneling microscope (STM).^[2,3] Due to the reduced coupling strength between local spin and conduction electrons on a metallic surface, the Kondo temperature is usually lower than that in bulk alloy system.^[4,5]

Recent experiments^[6–10] revealed that the Kondo temperature for a single magnetic molecule on metal surface is much higher compared to a single atom. In the case of individual manganese phthalocyanine (MnPc) molecules adsorbed on the top of Pb islands, oscillating Kondo temperatures were observed and attributed to the formation of the thickness-dependent quantum well states in the host Pb islands, which can dramatically change the electronic density of states of the host around the Fermi level.^[9] On the other hand, two-dimensional molecular Kondo systems are also very interesting because the self-assembled magnetic molecules may act as templates for fabricating molecular spintronics devices. In this study, we prepare the self-assembled monolayer (SAM) of MnPc molecules on Pb islands and investigate the Kondo effect systematically by using LT-STM. Because the different adsorption sites of molecules in the SAMs enable us to change the coupling strength between the MnPc molecules and the Pb substrate, the variation of the Kondo temperatures is observed. We find the width of the d_{xy} orbital of Mn ion plays an important

role in controlling the Kondo temperature in such two-dimensional systems.

Our experiments were conducted in a Unisoku UHV He3 STM system with the base pressure of 1.2×10^{-10} Torr. The sample preparation has been described in detail elsewhere.^[9] The SIC reconstruction phase^[11,12] of Pb/Si(111) was obtained by deposition of 2–3 ML Pb on the clean Si(111)- 7×7 surface followed by annealing at 280°C for 10 s. After another 9 ML Pb deposition on the SIC phase and further annealing for half an hour, flat-top Pb(111) islands were formed. Submonolayer MnPc molecules were then evaporated to the sample at 77 K. Room temperature annealing can lead to the formation of a self-assembled monolayer of MnPc on the Pb island surface. All the STM experiments were conducted at 4.2 K and the PtIr tips were used. In order to avoid the complexity of the interaction between Kondo impurity and superconductivity, 3 T magnetic field was applied to completely quench the superconductivity of the Pb substrate.

Figure 1(a) shows the differential scanning tunneling spectra (dI/dV) of a 12 ML Pb(111) surface, which was chosen as the host metal for the following experiments. In the spectra, two sharp peaks are located at -0.5 V and $+0.27$ V, corresponding to the highest occupied quantum well state and the lowest unoccupied quantum well state, respectively. Governed by both the molecule-molecule and the molecule-substrate interactions,^[13] the MnPc molecules self-assemble into ordered monolayers with a square lattice pattern forming a 4×4 superstructure on the Pb(111) island, as shown in Fig. 1(a). The square lattice, which is determined by the four-fold geometry of the MnPc molecule (see the inset in Fig. 1(a)), indi-

*Supported by the National Natural Science Foundation of China under Grant Nos 20733008 and 10904168, and the National Basic Research Program of China under Grant No 2009CB929404.

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cates a relatively weak interaction with the three-fold symmetry substrate. The weak interaction is further demonstrated by the fact that the molecules can be easily dragged out from the edge of molecular islands on the Pb island surface by an STM tip.^[9] The high resolution STM image in the inset of Fig. 1(b) reveals that the close-packing direction of the molecules is rotated by 12° with respect to the [110] direction of the substrate, as indicated by the white lines in Fig. 1(b).

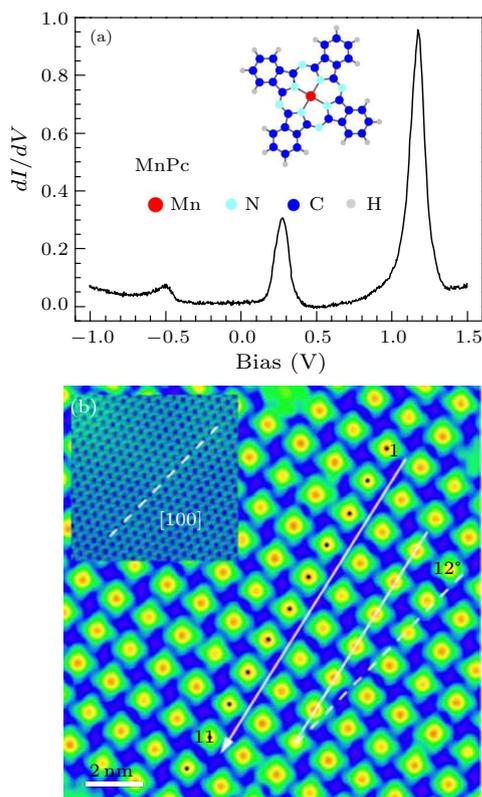


Fig. 1. (a) The dI/dV spectra acquired from 12 ML Pb island. The inset shows the molecule structure of the MnPc. Tunneling condition: $V = 0.6$ V, $I = 0.1$ nA. (b) STM image ($15 \text{ nm} \times 15 \text{ nm}$) of the self-assembled MnPc monolayer on Pb island surface. Tunneling conditions: $V = -0.3$ V, $I = 0.2$ nA. The inset shows the atomic resolution image of the Pb island surface near the molecule island. Note that the close-packing direction of the molecules is rotated by 12° with respect to the [110] direction of the substrate.

The Kondo temperature, which characterizes the spin-electron coupling strength, can be determined by the width of the resonance around the Fermi level in the dI/dV spectra. To do this, we positioned the STM tip above the center of a MnPc molecule, where the magnetic Mn ion is located, to acquire the dI/dV spectra. Figure 2(a) shows the dI/dV curves of the MnPc molecules, which are labeled from 1 to 11 in Fig. 1(b). For each of the molecules, an pronounced peak at the Fermi level is observed, which is attributed to the Kondo resonance caused by the interaction between d_{xy} orbital of the Mn ion and the conduction electrons.^[9] Another important observation here is the

width of the Kondo resonance, which changes from molecule to molecule. For example, the widths of the Kondo resonance for the molecules 4, 5, 6, and 7 are larger than those for other seven molecules. As we know, the width of the Kondo resonance is directly associated with the Kondo temperature via the formula:^[14]

$$\delta_{\rho R} = \frac{[\text{Im}G_{R,\sigma}^{(0)}(\omega - i\delta)]^2}{\pi\rho_0} \left\{ \frac{2qR\varepsilon + q_R^2 - 1}{\varepsilon^2 + 1} + C_R \right\}, \quad (1)$$

$$\varepsilon = \frac{\omega - \varepsilon_K}{T_K}, \quad (2)$$

where q , T_K and ε_K represent the line-shape parameter, the Kondo temperature, and the energy shift to the Kondo resonance, respectively. Fitting of the curves in Fig. 2(a) with the above formula yields the Kondo temperature, which varies in a wide range from 50 K to 300 K, and will be discussed in the following. This fact suggests a dramatic change in the spin-electron coupling strength between different molecules and the Pb substrate. It is worthy to mention that during the fitting process, we found that the width of the Kondo resonances observed here are much larger than the Zeeman splitting in the 3 T magnetic field.^[9] The influence of the magnetic field on the Kondo resonances can be neglected.

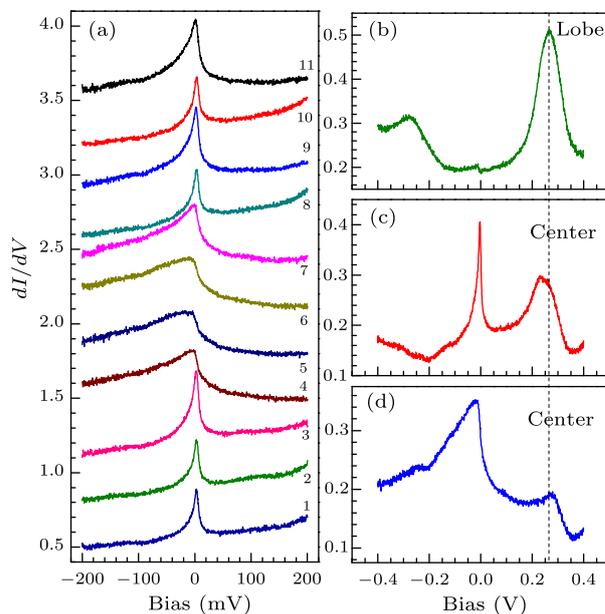


Fig. 2. (a) dI/dV spectra on the center of the MnPc molecules labeled from 1 to 11 in Fig. 1(a). Tunneling condition: $V = 0.1$ V, $I = 0.5$ nA. (b) dI/dV spectrum on the center of molecule with wide Kondo resonance. (c) dI/dV spectrum on the center of molecule with narrow Kondo resonance. (d) dI/dV spectrum on the lobe of the molecule showing strong quantum well states of the substrate. Tunneling conditions for (c)–(d): $V = 0.157$ V, $I = 0.4$ nA.

The scattering of the Mn ion in the MnPc molecule will modify the electron states of the substrate. To ob-

tain more information about the interaction between the substrate and the molecules with different Kondo temperatures, the dI/dV spectra at a wider energy range (-0.4 eV to $+0.4$ eV) were recorded and shown in Figs. 2(b) and 2(c). As shown in Fig. 2(b), for a molecule with larger width of the Kondo resonance, the quantum well state peak around 0.27 eV of Pb is almost completely suppressed. This means stronger scattering of the Mn ion in the MnPc molecule with higher Kondo temperature. In comparison, the molecule with narrower Kondo resonance shows less scattering, and the suppressing of the quantum well state is not strong (Fig. 2(c)). We also recorded the dI/dV spectra when the tip was located on the lobes of a MnPc. Due to the absence of scattering center, the strong quantum well state peak was observed, indicating much smaller scattering effect on the substrate (Fig. 2(d)).

Several possible mechanisms may cause the variation of Kondo temperatures in the MnPc SAMs: the formation of two-dimensional spin network, the reduction of density of states by the nearest-neighboring molecules, and different adsorption sites. First, the possibility of the two-dimensional spin network can be excluded since the spin coupling usually quenches the Kondo resonance.^[15,16] Moreover, there is no spin coupling channel in the single layer MnPc film. The superexchange channel can only be established in molecular multilayer structures.^[17] In general, reduction in the density of states by the nearest-neighbor molecule often weakens the Kondo resonance inside two-dimensional self-assembled molecule thin film.^[7] However, in our experiment, although the numbers of the nearest-neighbors are the same for all the molecules, as shown in Fig. 1(b), the Kondo resonance widths are different from each other. Thus this effect can also be excluded.

In theory,^[18] the Kondo temperature is determined by the density of the conduction electron ρ and the exchange coupling J at the magnetic impurity site as $T_K \propto e^{-1/\rho J}$. In the Anderson Model, $\rho J \sim \Delta \left(\frac{1}{|\varepsilon_d|} + \frac{1}{|U+\varepsilon_d|} \right)$, where ε_d is the energy level of the d orbital, U is the coulomb energy, and Δ is the width of the d orbital. Both the d orbital level and the width could contribute to the variation of the Kondo temperature. The d_{xy} orbital can not be directly observed in the differential conductance spectra, probably due to the fact that the d_{xy} orbital is far from the Fermi level. However, the molecular orbital mediated tunneling was observed on the lobe around 0.27 eV below the Fermi level. The width of this peak defines the coupling strength between the molecule and the substrate:^[19] the larger the width, the stronger the coupling strength. Figure 3(a) shows the dI/dV spectra on the lobes of three molecules (a, b, c). The first peak around -0.5 V has the same energy level, since they come from the quantum well state of the sub-

strate (see the dashed line in Fig. 3(a)). However, the position and width of the second peak, which comes from the molecule orbital on the lobe, change for different molecules. By taking the dI/dV spectra at the center of three molecules (a, b, c), we obtained the corresponding Kondo resonance peaks at the Fermi level, as displayed in Fig. 3(b). For molecule *a* with a narrow Kondo resonance, the peak of the molecule orbital is also narrow and far from the Fermi level; for the molecules *b* and *c* with wider Kondo resonance, the peak is wider and closer to the Fermi level. Considering that both the d_{xy} orbital and the molecule orbital on the lobe are parallel to the surface, we expect that the shift and the width of both orbitals have the same order, i.e., $\delta\varepsilon_d \sim \delta\varepsilon_{MO}$, and $\Delta_d \sim \Delta_{MO}$. From the measurement of many molecules, we found $\delta\varepsilon_d \sim \delta\varepsilon_{MO} \sim 0.05$ eV. Since $|\varepsilon_d|$ and $|U + \varepsilon_d|$ are in the eV range, the second term $\frac{1}{|U+\varepsilon_d|}$ is almost constant for the different molecules. Thus the variation in the Kondo resonance is mainly due to change in the width of the d_{xy} orbital. From previous assumption, we can deduce $\ln(T_K) \propto A - B \frac{1}{\Delta_d} \approx A - B \frac{1}{\Delta_{MO}}$, where T_K is the Kondo temperature. It is found that T_K and Δ_{MO} are in agreement with this relation (Fig. 3(c)). Obviously, the change in d_{xy} orbital width comes from different bonding strengths at different adsorption sites of MnPc. Similar observation was reported in FePc on Au(111).^[10]

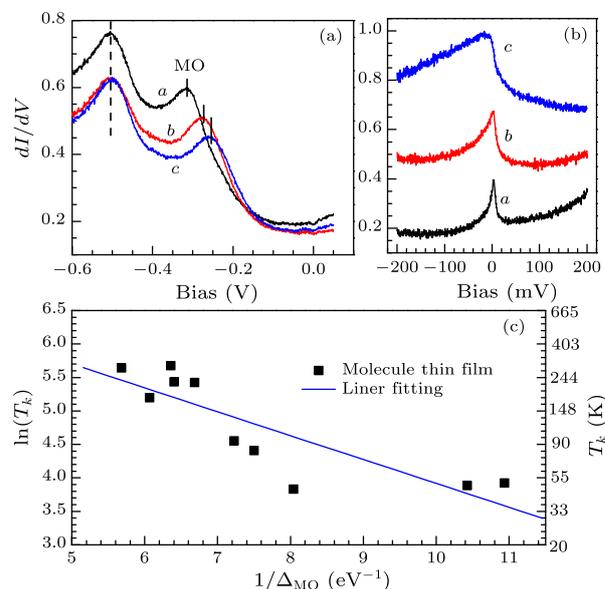


Fig. 3. (a) dI/dV spectra on the lobe of three different molecules a, b, and c, showing the quantum well state at 0.5 eV below the Fermi level. The second peaks in the spectra come from the molecule orbital on the lobe. Tunneling condition: $V = -0.3$ V, $I = 0.5$ nA. (b) dI/dV spectra at the center of three different molecules, showing the Kondo resonance at the Fermi level. Tunneling condition: $V = 0.1$ V, $I = 0.5$ nA. (c) The relationship between $\ln(T_K)$ and $1/\Delta_{MO}$. The dots are the experiment data, the line is the numerical fitting result.

In order to give an illustrative characterization for the variation of the Kondo resonance, the dI/dV mapping at -0.05 V was carried out. Figures 4(a) and 4(b) show the topographic image and the corresponding dI/dV mapping image, respectively. The spatial distribution of the Kondo resonance modulation can be clearly illustrated. Here, the yellow dots show the molecules with higher Kondo temperatures and with larger widths of the Kondo resonance, while the blue dots show the molecules with lower Kondo temperatures. By comparing to the dI/dV spectra shown in the inset of Fig. 4(b), we find the values of dI/dV at -0.05 V and the widths of the Kondo resonance are highly correlated.

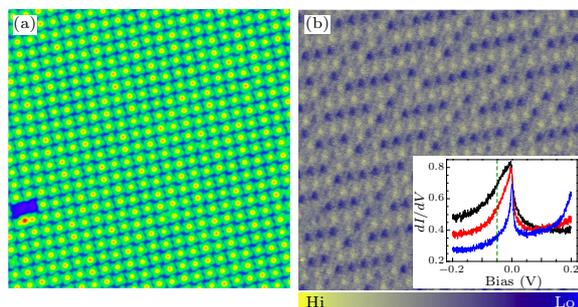


Fig. 4. (a) STM image ($30\text{ nm} \times 30\text{ nm}$) of the self-assembled MnPc on 12 ML Pb island surface. Tunneling condition: $V = -0.05\text{ V}$, $I = 0.3\text{ nA}$. (b) dI/dV mapping at -0.05 V . The inset shows the typical Kondo resonances with different widths in the image.

In summary, we have systematically studied the Kondo resonance in the MnPc self-assembled monolayers on the Pb(111) surface and investigated the Kondo temperature variation at the 50–300 K range.

The dI/dV spectra of the molecular orbital reveal that this variation mainly originates from the width change of d_{xy} orbital of the Mn ion at different adsorption sites rather than the energy level shift of the orbital. In addition, the suppression of the quantum well states directly shows that the molecule with higher Kondo temperature has stronger scattering effect to the substrate electron. The present work provides the important information on the molecule-substrate interaction of the self-assembled thin film at the single molecule level, which is essential for understanding and controlling the interaction between the spin and the environment in the potential molecular spintronics application.

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