

論文の内容の要旨

論文題目 Interplay between geometrical and electronic structure within the two dimensional surface lattice probed by iron phthalocyanine
(鉄フタロシアニン表面二次元格子中の構造と電子状態の相関)

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1. Introduction

Magnetism of thin and small materials is being interested in since it is related to the degree of integration in the electronic devices. Besides, there are interfaces between the electrodes and the elements of the electronic devices. Thus, nanoscale thin films or structures suffer from the effect of the electrodes. Effect of substrate on magnetic thin film is studied extensively [1]. In the current work, we focus on thin films of magnetic *molecules*. Since crystal structure of molecules are determined by rather weak interaction like van der Waals interaction, geometrical structure as well as electronic structure should be strongly affected by the interaction with the substrate. Scanning tunneling microscope (STM) has distinct ability to evaluate both geometrical and electronic structure with high spatial and energy resolution. Recently, spin state of single atoms or molecules adsorbed on metal substrate are studied through observation of spin excitations [2,3] or Kondo resonance using STM [4,5]. Investigating molecular film by STM will allow us to obtain information on relation between the local geometrical and electronic structure.

We adopted iron phthalocyanine (FePc) as a probe molecule for investigating the relationship between the geometric and electronic structure inside thin molecular film. FePc is a magnetic molecule which has $S = 1$ in bulk [6]. It has a characteristic planar cross shaped [7], which makes identification of its orientation from STM image easy. The effect of the species and the orientation of the substrate on thin film of magnetic molecule is investigated by using STM and FePc.

2. Experimental

All experiments were carried out in an ultra-high vacuum system. Ag(111), Ag(110), Ag(100) and Au(111) single crystal surfaces were used as substrates. A substrate was first cleaned by sputtering and annealing, and cooled down to room temperature. Then, FePc molecules were sublimed onto the substrate. The sample is then cooled down to 400 mK – 6 K and was provided for the measurement using STM. Magnetic fields up

to 7 T (11 T) were applied parallel (perpendicular) to the substrate respectively. Lock-in technique was used to measure dI/dV spectra (I : tunneling current, V : bias voltage of the sample against the tip).

3. Iron phthalocyanine / Ag(111), Ag(110), Ag(100), spin and vibration excitations

FePc molecules directly adsorbed on Ag(111), Ag(110), Ag(100) surfaces didn't show any signals from Kondo effect nor spin excitation. The spin of FePc molecules seems to be quenched because of electron transfer between the substrate and the molecules. As the coverage increases, islands of the second layer molecules start to grow once the first layer molecules cover the surface of the substrate. dI/dV spectra obtained at the molecular center of the second layer molecules show signals from spin excitations. It is reported that thin oxide layer between molecules and a metal substrate act as a buffer layer to retain magnetic moment of the molecules [3]. In our case, the first layer molecules seem to play the role to prevent interaction between the second layer molecules and the substrate. Similar situation is reported for cobalt phthalocyanine molecules adsorbed on Pb/Si(111)-(1×1)-Pb [8]. Second layer molecules in several different local environment appear when the coverage is over monolayer; the adsorption site of the ground first layer molecules, the rotation angle of the second layer molecules from the first layer molecules, the number of neighboring molecules are different depending on the molecules. The zero field splitting of the second layer molecules took various values reflecting various local environment of the molecules, though, effect of each elements couldn't be identified so far.

In the dI/dV spectra of the second layer molecules, signals from vibration excitation were observed in addition to the spin excitation signals. The conductance changes due to vibration excitations were especially large for Ag(111) and Ag(100). The enhancement of the conductance change due to vibration excitation for the second layer molecules is also explained by the electronic decoupling of the molecules from the substrate in the frame work of resonant tunneling model. In this model [9], the electrons tunnels out from the STM tip to a molecules induces a tentative anion state in the molecule. The molecules feel the potential change tentatively and deform. While the residence time of the electron is limited, the molecule is left over in a vibrationally excited state. The difference in the spectra between the first layer molecules and the second layer molecules are qualitatively explained by the short life time of the anion state for the first layer molecules which is caused by strong interaction between the first layer molecules and the substrate [10]. The existence of a strong bonding interaction between the first layer molecules and the Ag(111) surface is confirmed from vibrational

energy shift of the first layer molecules by using electron energy loss spectroscopy [11].

4. Iron phthalocyanine / Au(111) , magnetic response of a Kondo lattice

In the low coverage regime, FePc molecules adsorb with their molecular plane parallel to the surface, isolated from each other. dI/dV spectrum obtained at the center of each isolated molecules shows narrow single dip around the Fermi level. The dip is assigned to Kondo resonance arising from 3d electron of iron [12,13]. At higher coverage, molecules assemble into clusters lining up in a lattice form. dI/dV spectra of the molecules in the clusters are modified from those of isolated molecules; the dip broadens for a small cluster, while it becomes double dip for large clusters [12]. Anti-ferromagnetic Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction between neighboring molecules is considered as the cause of the spectral change [12].

As such, FePc molecules in a form of lattice on Au(111) is proved to be the Kondo lattice system in which magnetic moments of Fe 3d electrons are periodically arranged. Kondo lattice system is expected to have many types of ground states depending on the competition between Kondo effects and RKKY interaction; while Kondo effect favors magnetically disordered state, RKKY interaction prefers magnetically ordered state [14]. We investigated dependence of the spectra of FePc lattice on Au(111) on the amplitude and direction of applied magnetic field, and revealed its ground state.

The measurement were conducted at the coverage where a molecular cluster consists of more than 9×9 is formed. Without the magnetic field applied, all molecules show double dip structure in dI/dV spectra. The response of the spectra to magnetic field depends on the direction of the magnetic field. FePc molecules orient in the direction with one diagonal pair of its benzene rings facing perpendicular to $[1\bar{1}0]$ direction of the substrate. The direction is signified as x in the text below. The other pair of diagonal benzene rings is parallel to $[1\bar{1}0]$ direction, and is signified as y. The direction perpendicular to the molecular plane (and substrate) is z. When the magnetic field is applied parallel to x direction, the spectral response is different for every other molecules; at 3T, molecules in line show single dip and double dip alternately. At 5T, all molecules show single dip. Under magnetic field of y direction, dI/dV spectra show almost no change below 5 T. When magnetic field is applied parallel to z direction, the amplitude of double dip was suppressed with increasing the magnetic field. The site dependence of the spectra against magnetic field in x direction indicates that the magnetic moment align parallel or anti-parallel to x direction at each site, and prove the formation of antiferromagnetically ordered ground state.

5. Summary

We examined geometric and electronic structures and their relationship of FePc molecules adsorbed on Ag(111), Ag(110), Ag(100) and Au(111) surfaces, and found following. The first layer FePc molecules adsorbed on Ag(111), Ag(110) and Ag(100) surface don't show signature of spin excitations nor Kondo resonance. The spin of those molecules seems to disappear because of interaction with the substrate. The second layer FePc molecules adsorbed on Ag(111), Ag(110) and Ag(100) surface show signature of both spin and vibration excitations in dI/dV spectra. FePc lattice on Au(111) surface shows modification of the spectra with $\sqrt{2} \times \sqrt{2}$ period under magnetic field, which proves anti-ferromagnetic ordering of the system.

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