

Site-Specific Kondo Effect at Ambient Temperatures in Iron-Based Molecules

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Kondo resonances are a very precise measure of spin-polarized transport through magnetic impurities. However, the Kondo temperature, indicating the thermal range of stability of the magnetic properties, is very low. By contrast, we find for iron phthalocyanine a Kondo temperature in spectroscopic measurements which is well above room temperature. It is also shown that the signal of the resonance depends strongly on the adsorption site of the molecule on a gold surface. Experimental data are verified by extensive numerical simulations, which establish that the coupling between iron states and states of the substrate depends strongly on the adsorption configuration.

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Because of their importance in the emerging field of molecular electronics the transport properties of single molecules have been the focus of intensive research, leading to the concept of a single-electron transistor [1] and a proof of principle of field regulation by external charges [2]. The magnetic properties of transition metal atoms in a host molecule can be detected by a Kondo resonance in cryogenic scanning tunneling microscopes [3–5]. These properties are important variables in the fabrication of single molecule devices [6–10]. Most previous studies of the Kondo effect focused on magnetic atoms on open metal surfaces [11–21]. However, the Kondo temperature in these systems is very low; the spin-dependent transport properties are consequently lost in an ambient environment. Recent studies of molecular Kondo effects show that caging the magnetic atoms in a molecule can elevate [3,4,22] or decrease [5,22] the Kondo temperature. In this case, both the molecular structure [4,5] and the molecular conformation [3] play an important role. Here, we present measurements of the Kondo effect of iron phthalocyanine (FePc) molecules on an Au(111) surface. The results are significant for two reasons. First, they indicate a high Kondo temperature, well above room temperature, for the FePc molecule adsorbed on Au(111) surface. This is in marked contrast to the low Kondo temperature for isolated Fe atoms adsorbed on the same surface [17]. Second, they reveal a substantial change of the effect with the adsorption configuration of the molecule. This indicates that magnetic properties of an interface can be controlled at the molecular level by site-specific adsorption.

The scanning tunneling microscopy (STM) experiments were performed on an Au(111) single crystal surface, prepared carefully by repeated cycles of Ar⁺ sputtering and annealing in ultrahigh vacuum (base pressure 3×10^{-10} mbar). FePc molecules were evaporated from the sublimation cell onto the gold surface at a temperature of ~ 370 K. Then the sample was transferred *in situ* into an

Omicron low-temperature STM operating at 4.6 K. The bias voltage is applied to the sample. dI/dV spectra were measured using a lock-in technique with a modulation signal (4 mV_{rms}, 1 kHz). The tungsten tip has been carefully prepared before spectroscopic measurements to ensure no tip-related features on the recorded dI/dV spectra. A topographic image of the Au(111) surface, covered by $\sim 2 \times 10^{13}$ per cm² FePc molecules, is shown in Fig. 1. The image of a single FePc molecule is a “cross” with a bright spot at the center, indicating a flat-lying adsorption configuration. The enhanced brightness at the molecular

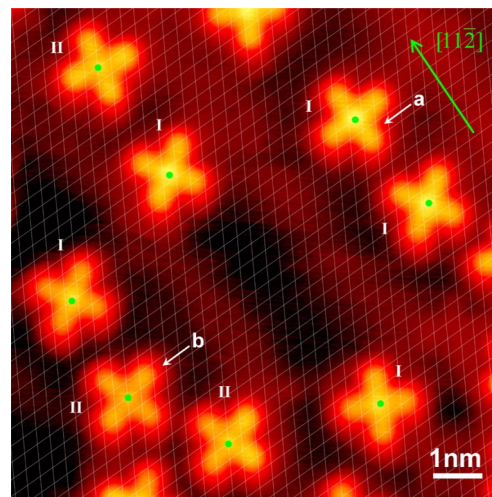


FIG. 1 (color online). STM image of isolated FePc molecules on Au(111) surface. Scanning parameters: $10 \text{ nm} \times 10 \text{ nm}$, $U = -0.5 \text{ V}$, $I = 69 \text{ pA}$. The direction of the Au(111) substrate is determined by surface reconstruction. The overlaid grid represents the gold substrate lattice, showing a shift of $1/2$ unit cell between the adsorption sites of the two types (I and II) of molecules. The dI/dV curves in (a) and (b) of Fig. 2 are measured at the center of molecules marked with (a) and (b), respectively.

The difference in the line shape of Kondo resonance between configuration I and configuration II is caused by the different competition between two electron tunneling channels. Within the Fano theory the line shape of the dI/dV spectra for a Kondo resonance is determined by the line shape parameter q [26]. q describes the ratio of the probability for tunneling through magnetic impurity orbitals, and tunneling directly into the surrounding conduction band. Our experimental results shows that configuration I ($q = 2.20$) has a much larger q value than configuration II ($q = 0.12$). In the FePc/Au(111) system, the first tunneling channel is via the d orbitals of the central Fe atom; the second channel is directly tunneling into the conduction band of the surrounding conduction electrons both on the gold substrate and within the FePc molecules. First, the molecular bonding to the substrate is stronger for configuration II than for configuration I, so it is much easier for the STM tip to detect the conduction electrons in configuration II than in configuration I. More electrons tunnel directly into the conduction band in configuration II than in configuration I. Secondly, the tunneling through central Fe atom is much decreased in configuration II compared to configuration I, which is obvious from low-bias STM images. In Fig. 1, the brightness of the central Fe atom for configuration II is much lower than that for configuration I. Therefore, different adsorption configurations have induced different interaction between d orbitals and the substrate, which influences the electron tunneling through the central Fe atom. Compared to configuration I the electron transfer directly into the conduction band is increased, and the transfer through the central Fe atom is decreased in configuration II, accounting for the large difference in the line shape of the Kondo resonance.

In summary, we have observed an unusually high Kondo temperature in the FePc/Au(111) system at the single molecular scale using LT-STM/STS. Our results show that both the Kondo temperature and the line shape of dI/dV spectra are greatly influenced by molecular adsorption configuration on the Au(111) substrate. This implies that it is feasible to control the local spin coupling and the competition between different tunneling channels in molecular Kondo effect by changing the molecular adsorption configuration. Given that the lateral structure of a molecular interface can be modified by the attachment of ligands [39], the finding opens up the possibility to tailor magnetic properties of an organic interface to the desired specifications.

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Multiple-impurity Anderson model for quantum dots coupled in parallelR. Žitko¹ and J. Bonča^{1,2}¹*Jožef Stefan Institute, Ljubljana, Slovenia*²*Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia*

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The system of several (N) quantum dots coupled in parallel to the same single-mode conduction channel can be modeled as a single-channel N -impurity Anderson model. Using the generalized Schrieffer-Wolff transformation we show that near the particle-hole symmetric point, the effective Hamiltonian in the local moment regime is the N -impurity $S=1/2$ Kondo model. The conduction-band-mediated RKKY exchange interaction between the dots is ferromagnetic and at intermediate temperatures locks the moments into a maximal spin $S=N/2$ ground state. We provide an analytical estimate for the RKKY interaction. At low temperatures the spin is partially screened by the conduction electrons to $N/2-1/2$ due to the Kondo effect. By comparing accurate numerical renormalization group results for magnetic susceptibility of the N -impurity Anderson model to the exact Bethe ansatz results of a $S=N/2$ SU(2) Kondo system we show that at low-temperature the quantum dots can be described by the effective $S=N/2$ Kondo model. Moreover, the Kondo temperature is independent of the number of impurities N . We demonstrate the robustness of the spin $N/2$ ground state as well as of the associated $S=N/2$ Kondo effect by studying the stability of the system with respect to various experimentally relevant perturbations. We finally explore various quantum phase transitions driven by these perturbations.

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I. INTRODUCTION

The Kondo effect emerges as the increased scattering rate of the conduction band electrons at low temperatures due to the presence of magnetic impurities which induce spin-flip scattering. It leads to various anomalies in the thermodynamic and transport properties of the Kondo systems. It is usually described using simplified quantum impurity models such as the Kondo model and the Anderson model.¹ The quantum impurity models attract the interest of the solid-state physics community both due to their unexpectedly complex behavior and intrinsic beauty, as well as due to their ubiquitous applicability to a vast array of physical systems such as bulk Kondo systems, heavy-fermion compounds and other strongly correlated systems,² dissipative two-level systems,³ single magnetic impurities, and quantum dots.⁴⁻⁶

After the properties of single-impurity models were unraveled using a complementary set of techniques (the scaling approach, Wilson's numerical renormalization group, Bethe ansatz solution, and various large- N expansion schemes),² the attention has increasingly focused to multiple-impurity models. Research in this field has recently increased due to a multitude of experimental results made possible by advances in micro- and nanotechnology. The multiple-impurity magnetic nanostructures under study are predominantly of two kinds: clusters of magnetic adsorbates on surfaces of noble metals (Ni dimers,⁷ Ce trimers,⁸ molecular complexes⁹) and systems of multiple quantum dots.¹⁰⁻¹⁴

The most important additional element that emerges in multiple-impurity models is the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction.¹⁵ It arises when the magnetic moments on the impurities induce spin polarization in the conduction band which leads to magnetic coupling of moments that are separated in space. The RKKY interaction depends on the interimpurity distance and can be either ferromagnetic or antiferromagnetic.

The competition between the antiferromagnetic RKKY interaction and the Kondo effect in two magnetically coupled local moments leads to a quantum phase transition at $J \sim T_K$ between strongly bound local magnetic singlet for $J \gg T_K$ and two separate Kondo singlets for $J \ll T_K$.¹⁶⁻²⁰ The role of the antiferromagnetic exchange interaction was also studied in the context of double quantum dots (DQD).²¹⁻²⁵ Two mechanisms can contribute to the effective exchange interaction between the dots: the conduction-band mediated RKKY interaction and the superexchange mechanism due to interdot electron hopping. Depending on the setup (serial or parallel embedding of the dots between the source and drain leads), either or both mechanisms may be significant. In magnetically coupled dots, embedded between the leads in series, the conductance is low for small exchange coupling when the Kondo singlets are formed between each dot and adjacent lead. Conductance is also low for large exchange coupling, when a local singlet state forms between the moments on the dots. In contrast, the conductance reaches the unitary limiting value of $2e^2/h$ in a narrow interval of J , such that $J \sim T_K$.^{21,22} The introduction of additional electron hopping between dots breaks the quantum critical transition, nevertheless, some signatures of the quantum phase transition remain detectable.²²

Strong ferromagnetic RKKY interaction between two magnetic impurities coupled to two conduction channels leads to three different regimes. At temperatures comparable to RKKY interaction, ferromagnetic locking of impurity spins occurs; this is followed by a two-stage freezing out of their local moment as they become screened by the conduction electrons.²⁶ This scenario was corroborated by numerical studies of the two-impurity Kondo model²⁷ and the Alexander-Anderson model.²⁸ Antiferromagnetic and ferromagnetic RKKY interactions lead to different transport properties of DQD systems.^{29,30} Due to recent advances in nanotechnology, the effects of RKKY interaction on transport properties became directly observable.¹³ Conductance

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Dephasing of conduction electrons by magnetic impurities in Cu/Ni and Cu/Cr samples: Influence of spin-glass transition on the superconducting proximity effect

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The dependence of the superconducting proximity effect on the amount of magnetic impurities in the normal part of Andreev interferometers has been studied experimentally. The dephasing rates obtained from fitting experimental data to quasiclassical theory of the proximity effect are consistent with the spin flip scattering from Cr impurities forming a local moment in the Cu host. In contrast, Ni impurities do not form a local moment in Cu and as a result there is no extra dephasing from Ni as long as Cu/Ni alloy remain paramagnetic.

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I. INTRODUCTION

Electron dephasing has been one of the most important problems of mesoscopic physics since its emergence in the 1980s. The main sources of dephasing have been identified as inelastic scattering due to electron-electron and electron-phonon interactions and scattering by magnetic impurities.¹ These have been carefully studied experimentally using the weak localization correction to the conductance of mesoscopic structures.² The topic has received renewed interest since the proposal of quantum computing (see, e.g., Ref. 3). Dephasing is one of the major obstacles in building a working solid-state quantum bit. Practically, the phase breaking time τ_ϕ is often limited by the presence of even tiny amounts of magnetic impurities.^{4,5}

The mechanism of dephasing by magnetic impurities has been studied extensively using weak localization⁶ and the suppression of the superconducting critical temperature.⁷ The dephasing rate in these experiments has been identified with the spin-flip rate obtained from the low temperature logarithmic increase in resistivity, the Kondo effect.⁸ Theoretically the problem of conductance in mesoscopic systems with magnetic impurities has been studied in various ranges of temperature and impurity concentration.⁹⁻¹² Recently, the effect of Kondo impurities on the superconducting proximity effect has been addressed qualitatively in the Au/Fe system.¹³

Here we present an experimental study of the effect of the magnetic impurities on the coherent part of the conductance of a normal metal in proximity to a superconductor. We have investigated a wide range of Kondo temperatures T_K for the two chosen systems $T_K \approx 10$ K for Cu/Cr and $T_K \approx 1000$ K for Cu/Ni.¹⁴ The dephasing rate obtained by fitting amplitude of resistance oscillations with magnetic field to the quasiclassical theory of the proximity effect (see Ref. 15 for a review on the superconducting proximity effect) in both cases is compared to the spin-flip rates estimated from Kondo effect.

II. SAMPLE FABRICATION

The samples were fabricated using *e*-beam lithography and standard processing. The geometry of the structures is

shown in Fig. 1. I_1 and I_2 are current leads; V_1 and V_2 , are voltage leads. The distance between the *N/S* contacts is about 150 nm, the length of normal wire between the voltage probes is $L=2.6 \mu\text{m}$. The area of superconducting loop is about $12 \mu\text{m}^2$. The first layer was the normal part, 40-nm-thick Cu/Ni or Cu/Cr alloy. The alloy films of various concentrations were fabricated by simultaneous evaporation of Ni or Cr and Cu at fixed rates to obtain the required concentration. To obtain clean interfaces between the layers, the contact area was Ar^+ plasma etched before the deposition of the second (superconducting) layer which was 60-nm-thick Al film. In case of Cu/Ni samples the resulting composition of the film was measured using x-ray spectroscopy in a scanning electron microscope with an accuracy

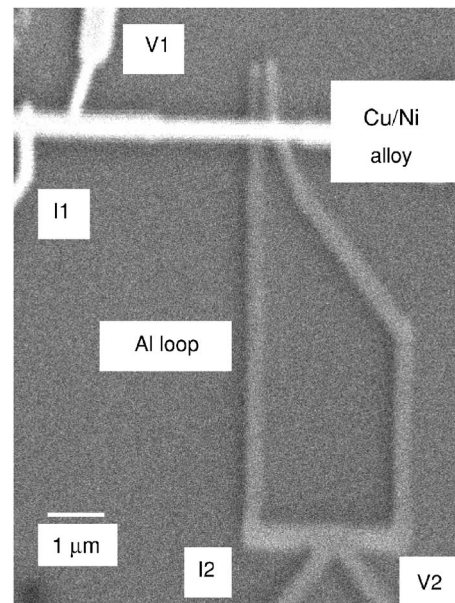


FIG. 1. SEM micrograph of a measured sample. Current contacts are labeled I_1 and I_2 ; voltage contacts V_1 and V_2 . The area of superconducting loop is $12 \mu\text{m}^2$.

$$\tau_{\phi}^{-1} = \tau_{SF}^{-1} \frac{2}{\left(1 + \frac{\alpha T_{SG}}{2T}\right)^2}, \quad (15)$$

where $\alpha=1.85$ for $S=3/2$ and denominator in right-hand side of Eq. (15) accounts for the reduction of dephasing due to the spin-glass transition at the temperature T_{SG} . Substituting $\tau_{\phi}^{-1}=1.7 \times 10^{10} \text{ s}^{-1}$ for Cu/Cr sample with $c=14 \times 10^{-6}$ at $T=0.3 \text{ K}$ into Eqs. (14) and (15) one gets T_{SG} to be about 2 K in reasonable agreement with resistivity measurements shown in Fig. 5.

In conclusion, we have studied the dephasing of conduction electrons by magnetic impurities in Cu/Ni and Cu/Cr samples. Dephasing in Cu/Cr samples is associated with

spin-flip scattering due to the Kondo effect. Influence of spin glass transition on the superconducting proximity effect has been observed. Estimation of T_{SG} made using formulas for spin-flip rate and the dephasing rate are in agreement with experiment. The dephasing in Cu/Ni samples can be explained by the contribution of other magnetic impurities, such as Cr by comparison to results in Cu/Cr samples.

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Nonequilibrium STM model for Kondo resonance at a surface

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Based on a no-equilibrium scanning tunneling microscope (STM) model, we study Kondo resonance on a surface by self-consistent calculations. The STM tunneling spectra (dI/dV curves) of magnetic atoms on a surface have well-known Fano's line shapes consistent with STM tunneling spectra of $3d$ transition-metal atoms on a novel-metal surface. The resonance peaks in dI/dV curves are generally the mixing of Kondo resonance and the dip structures (zero-bias anomaly) observed also in a quantum dot system. The shapes of tunneling spectra are dependent on the energy range of tunneling electrons. Our results show that both energy cutoff and energy window of tunneling electrons have significant influence on the shapes of tunneling spectra. The method of self-consistent nonequilibrium matrix Green function is discussed in detail.

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I. INTRODUCTION

The scanning tunneling microscope (STM) has been widely used to study atomic and electronic structures of surface and atoms absorbed on it. A currently interesting topic is Kondo effect of magnetic atoms on a nonmagnetic metal surface. The interest along this direction is motivated by recent advances in the construction of a novel nanostructure device on surface. STM has been used to probe the Kondo resonance of a single magnetic atom.¹⁻⁶ The magnetic cobalt phthalocyanine molecule absorbed on Au(111) surface shows Kondo effect by having cut away eight hydrogens from the molecule.⁷ Kondo resonance has been found in other magnetic molecules absorbed on metal surfaces such as $\text{Co}(\text{CO})_n$ molecules on Cu(100) surface.⁸ Additionally, a STM has also been used to study the formation of Kondo molecules.^{9,10} The most interesting phenomenon is the so-called Quantum Mirage^{11,12} due to the refocus of Kondo resonance on surface.

Generally STM tunneling spectrum is not exactly correspondent to the atomic and electronic structure of the surface. To obtain the realistic atomic and electronic structure from STM tunneling spectrum, it is valuable to establish a believable STM theoretical model that is related the realistic atomic structure or electronic structure to the STM tunneling spectrum. Based on the Tersoff like theory,¹³⁻¹⁶ the differential conductance of electronic tunneling in STM is proportional to the local density of state (LDOS) of surface state. The resonance peak at zero-bias voltage in dI/dV curve is generally the mixing of Kondo resonance with other resonance such as d -resonance from a $3d$ magnetic atom.² The STM models based on the Anderson model have successfully explained the Fano shape of the Kondo resonance using the equilibrium many-body theory¹⁷⁻²¹ and nonequilibrium theory.²²

Quantum tunneling of electrons in a STM device is out of equilibrium in nature. In this paper, using a nonequilibrium self-consistent method, we calculate the STM tunneling spectra for magnetic atoms on metal surface. Kondo effect can be solved using analytical or numerical methods, such

as, the noncrossing approximations (NCA) and other larger N methods are suited for the infinite U Anderson model.²³⁻²⁵ The numerical renormalization group (NRG) and the exact Bethe ansatz need to linearize the dispersion relation near Fermi energy after having simplified into a one-dimension model.²³ The method used in this paper is similar to the iterative perturbation theory (IPT).^{26,27} The big difference is that in this work the Kondo resonance peak is decoupled from other parts of the Green function. However, for IPT, the Kondo resonance is imported into the Green function of magnetic atom by interpolating Σ_0^2 self-energy into an appropriate self-energy ansatz. The decoupled scheme in this work can be obtained by more detailed theoretical analysis such as in Ref. 28.

As a company of Kondo resonance, the so-called zero-bias anomaly has a contribution to the differential conductance near zero-bias voltage. The zero-bias voltage anomaly may have different origins such as the orthogonality catastrophe²⁹ and the cotunneling mechanism.^{30,31} The electrons do not have enough energy for most many-body events at small bias voltage. The zero-bias anomaly appears as a local minimum in dI/dV curves near zero-bias voltage.

Experimentally Kondo resonances in dI/dV curves are clear dip structures for single absorbed magnetic atoms¹⁻⁴ but peak structures for absorbed magnetic molecules.^{7,8} In this paper, the signals of Kondo resonance from the dI/dV curves are Fano line shapes and are the mixing of Kondo resonance and dip structure due to zero-bias anomaly. This is well-consistent with experimental observations. The zero-bias anomaly generally appears as a dip structure near zero bias and is frequently covered by background noise. If an other resonance peak appears at zero bias, the zero-bias anomaly can show itself by modulating the resonance peak. This is why Kondo resonance generally appears with a local minimum in dI/dV curves. If we properly reduce the background noise, the dip structure also can be observed in the tunneling spectra. The shapes of tunneling spectra are dependent on the energy range of tunneling electrons. The paper is organized as follows, after a brief introduction we present the theoretical STM model in Sec. II. In Sec. III, we present the nonequilibrium self-consistent method in detail. Our main

of the Kondo peak unchanged. The bias-voltage is applied by changing the chemical potential of the tip in our numerical calculations. μ_S keeps zero when applying a small bias voltage V_b on the surface mean that applying a bias voltage to the tip $V_t = -V_b$.

In real calculations, we add a minus in front of the current formulas Eq. (4), Eq. (7), and Eq. (8) to make the current

$J_t = J_1 + J_2 > 0$ at positive bias once the lower bound and upper bound of the integrals are clearly written in the current formulas. We can adopt the chemical potential language, just as in Ref. 39, without introducing additional minuses in the current formulas. The basic reason for the difference is that the increase of chemical potential $\delta\mu$ of electrons is equal to $-e \delta V_b$.

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Evolution of magnetism of Cr nanoclusters on Au(111): First-principles electronic structure calculations

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We have carried out collinear and noncollinear electronic structure calculations to investigate the structural, electronic, and magnetic properties of isolated Cr atoms, dimers, and compact trimers. We find that the Cr monomer prefers to adsorb on the fcc hollow site with a binding energy of 3.13 eV and a magnetic moment of $3.93\mu_B$. The calculated Kondo temperature of 0.7 K for the monomer is consistent with the lack of a Kondo peak in scanning tunneling microscopy (STM) experiments at 7 K. The compact Cr dimer orders antiferromagnetically and its bond length contracts to 1.72 Å close to the value for the free-standing Cr dimer. The very low magnetic moment of $0.005\mu_B$ for the Cr atoms in the dimer is due to the strong *d-d* hybridization between the Cr adatoms. Thus, these calculations reveal that the absence of the Kondo effect observed in STM experiments is due to the small local moments rather than the Kondo quenching of the local moments suggested experimentally. The Cr compact trimer exhibits noncollinear coplanar magnetism with vanishing net magnetic moment in agreement with experiment.

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I. INTRODUCTION

The study of magnetism at the nanoscopic scale is a major research activity in condensed matter physics. Nanomagnetism is a highly demanding fundamental problem as well as important for applications in high density recording media and memory devices. A particularly attractive feature of these systems is the strong sensitivity of their electronic and magnetic properties to the geometrical and chemical environment of the atoms. Consequently, numerous experimental studies have been concerned with the production and characterization of a large variety of nanometer scale magnetic materials involving transition metals and noble metals in different structural arrangements.¹

Magnetic transition-metal nanostructures on nonmagnetic substrates have attracted recently large attention due to their unusual magnetic properties.^{2,3} The supported clusters experience both the reduction of the local coordination number, as in free clusters, as well as the interactions with the electronic degrees of freedom of the substrate, as in embedded clusters, which may lead to the Kondo effect.⁴ The complex magnetic behavior is usually associated with the competition of several interactions, such as interatomic exchange and bonding interactions, the Kondo effect, and in some cases noncollinear effects, which can give rise to several metastable states close in energy.^{3,5,6} The ground state can, therefore, be easily tuned by an external action giving rise to the switching between different states.

Recent advances in scanning tunneling microscopy (STM) and the ability to build magnetic clusters with well-controlled interatomic distances on metal surfaces have opened the possibility of probing *local* interactions in magnetic nanostructures assembled atom by atom at surfaces.⁷⁻⁹

STM is ideal for studying the low-energy structure near the Fermi energy (E_F) since it allows access to states both above and below E_F . Recent STM studies have investigated the interplay between magnetic and electronic phenomena in one-impurity,⁷ two-impurity,⁸ and more recently, in three-impurity⁹ systems. Cr is unique among the transition-metal adatoms, because its half-filled valence configuration ($3d^54s^1$) yields both a large magnetic moment and strong interatomic bonding leading to magnetic frustration.^{10,11} The STM spectra for Cr clusters supported on the Au(111) surface can be summarized as follows.⁹ The lack of a Kondo peak for the single Cr atom was attributed to the fact that the Kondo temperature T_K is significantly less than the experimental temperature of 7 K. The featureless STM spectrum observed for the dimer⁸ was suggested to be due to the strong antiferromagnetic coupling between the atoms, which in turn quench the Kondo effect. Interestingly, compact triangular Cr trimers [Cr atoms occupying nearest-neighbor sites on the (111) Au surface] exhibited two distinct classes of behavior. In the first state, they displayed a featureless STM spectrum, whereas in the second they displayed a narrow resonance at the Fermi energy. Trimers were reversibly transferred from one state to the other by very small shifts of one atom via tip manipulation. It was suggested that the two observed states correspond to equilateral and isosceles trimer configurations, with a net trimer magnetic moment of zero and nonzero, respectively.

On the theoretical side, *ab initio* electronic structure calculations have been employed to study the collinear magnetic properties of 3*d* adatoms and clusters on the (001) Ag (Refs. 2 and 12) and Cu (Ref. 13) surfaces and the (111) Cu (Ref. 14) surface. The magnetic properties of small *free-standing* chromium clusters have been investigated by *ab*

TABLE IV. Calculated magnetic moments of an equilateral Cr trimer, in a noncollinear magnetic configuration, at the Au(111) surface, with spin-orbit coupling included. The orbital magnetic moments L_δ for $\delta=x,y,z$, the corresponding spin magnetic moments S_δ , and the total magnetic moment M are given in Bohr magnetons (μ_B).

Cr site	L_x	L_y	L_z	S_x	S_y	S_z	M
Cr1	0.00	-0.03	0.02	-0.00	3.17	-0.00	3.17
Cr2	0.02	0.01	0.02	-2.75	-1.58	-0.00	3.17
Cr3	-0.02	0.01	0.02	2.74	-1.58	0.00	3.14

tronic, and magnetic properties of monomer, dimer, and trimer Cr clusters on the Au(111) surface. Our results show that the fcc hollow is the most favorable location for the single Cr adatom and has a binding energy of 3.3 eV and a magnetic moment of $3.93\mu_B$. The Cr DOS for the majority (minority) spin state shows Lorentzian-shaped virtual states centered at E_d-E_F (E_d-E_F+U) ~ 0.5 eV (~ 2.5 eV) below (above) the Fermi energy. The calculated single Cr Kondo temperature of 0.7 K is consistent with the lack of a Kondo effect at 7 K in

STM experiments. The compact dimer is found to order antiferromagnetically, has a very short bond length of 1.72 Å, and a very low magnetic moment of $0.005\mu_B$. This is due to the strong $d-d$ hybridization between the Cr atoms. Thus, these calculations reveal that the lack of the Kondo effect observed in STM experiments is due to the small Cr magnetic moments rather than the Kondo suppression of the local moment, as has been suggested in the analysis of experiments. The results for the noncollinear triangular compact trimer predict that the net spin cluster magnetic moment is zero, consistent with the featureless spectrum of the STM study. Future work will be aimed at investigations of the linear trimer and isosceles triangle cases, as well as of collinear magnetism perpendicular to the surface.

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Scanning tunnelling microscopy and electronic structure of Mn clusters on Ag(111)

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ABSTRACT Small Mn clusters (Mn_1 – Mn_4) are prepared by manipulation of Mn adatoms on Ag(111) with the tip of a scanning tunnelling microscope. The apparent heights of the clusters are observed to increase monotonously from 1.6 Å for a monomer to 2.2 Å for a tetramer. Self-consistent calculations of the electronic structure of these clusters are in encouraging agreement with the experimental data.

PACS 73.22.-f

1 Introduction

Clusters of metal atoms on surfaces often exhibit intriguing electronic, magnetic, and catalytic properties [1]. A key issue in investigating these properties is the preparation of clean clusters on well-defined surfaces. For small cluster sizes, various properties exhibit marked size effects where the presence or absence of a single atom matters. A number of techniques for the preparation of mass-selected clusters are available and have been reviewed [2]. While techniques for “soft-landing” of such clusters are being used and developed the complexity of the required apparatus for producing substantial fluxes of clean, mass-selected clusters is considerable. Moreover, despite mass-selection before deposition, the possibility of fragmentation and of morphological changes and diversity have to be considered, as highlighted by, e.g., a low-temperature scanning tunnelling microscopy (STM) investigation of soft-landed, size-selected Si clusters on Ag(111) [3]. An alternative route is to use the tip of a STM to laterally move individual adatoms on a surface as to form clusters. This kind of “atom manipulation” has recently been used to construct dimers of Au, Mn, Fe and Co on NiAl(100) [4, 5], dimers of Ni on Au(111) [6], Cr trimers on Au(111) [7] and linear Au or Cu chains of up to 20 atoms on NiAl(100) and Cu(111) [8, 9]. Here we present experimental results concerning manipulation and imaging of Mn monomers to tetramers on Ag(111) along with preliminary account of ab-initio calculations of their electronic structure.

2 Experimental details

The experiments were performed with a custom-built ultra-high vacuum (UHV) STM which operates at a temperature of $T = 4.6$ K [10]. Ag(111) substrates were prepared by standard ion bombardment and annealing cycles in UHV. Approximately 0.1% of a monolayer of Manganese atoms were evaporated in UHV onto the cold Ag(111) substrate.

3 Experimental results

Manganese atoms on Ag(111) image as a protrusion of 1.6 Å height and 11 Å full width at half maximum (FWHM) at a sample voltage of $V = 1$ V (Fig. 1a) similar to previous observations of adatoms on noble metal surfaces [11, 12]. The STM images presented here have been recorded at a tunnelling current $I = 0.01$ nA, i.e., a resistance $R = 100$ GΩ. This fairly high resistance was used since tip sample interactions at tunnelling resistances of $R \approx 700$ MΩ already suffice to occasionally move atoms during a scan. Consequently, Mn adatoms can be easily moved on the surface with the STM tip following standard procedures [13–15]. An atom is moved by placing the tip over it at high tunnelling resistance (i.e., $R = 100$ GΩ), then changing the tunnelling

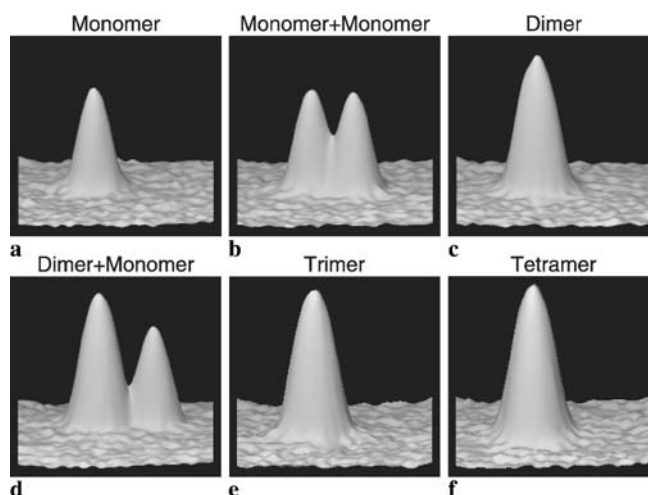



FIGURE 1 56×56 Å² constant current topographic scan of Mn atoms prior to and after manipulation. ($V = 1$ V, $I = 0.01$ nA, $R = 100$ GΩ)

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Kondo state of Co impurities at noble metal surfaces

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ABSTRACT We use scanning tunneling microscopy and spectroscopy to study the properties of magnetic Co adatoms on noble metal surfaces at 6 K. Due to spin-flip scattering of the substrate electrons at the impurity the many-body Kondo state forms. This state is characterized by an energy, the Kondo temperature T_K . We measure T_K of adatom systems and a resonant scattering phase shift locally and are thus able to discuss the coupling of the Co adatom to the metal electronic system. From the resonant scattering phase shift of the surface-state electrons scattering off a Co adatom on Ag(111), we find that the coupling to the surface state is rather weak. On the other hand, increasing the number of nearest neighbor substrate atoms increases the coupling of a Co adatom to the host metal and increases T_K . This shows the dominant character of the coupling of the Co atom to the bulk states of the substrate crystal.

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1 Introduction

The interaction of a magnetic impurity with the electrons of a non-magnetic host serves as a paradigm of many-body physics [1]. Interest into the classical Kondo effect has been renewed when it was shown that the properties of Kondo systems consisting of magnetic adatoms on metal surfaces can be studied by scanning tunneling microscopy (STM) [2, 3]. The Kondo state is formed by the interaction of the electronic spin on the adatom with the electron sea of the host metal. This interaction leads to a many-electron ground state where the host electrons screen the spin of the impurity [1]. The Kondo temperature T_K can be thought of as the binding energy of the correlated state (0..1000 K) and can be directly measured by low temperature scanning tunneling spectroscopy (STS). Provided that the temperature of the experiment T is low compared to T_K (as is the case for the results reported here) a resonance of width $2k_B T_K$ is formed in the density of states of the impurity atom at the Fermi energy E_F . This resonance shows up in the differential conductance of the tunneling contact dI/dV at the lateral adatom position (the STM tip being 5–10 Å away from the surface) as a Fano

resonance [2–5]. A number of different adsorbate-substrate systems have been investigated by now [6–14], but there is only little progress in understanding theoretically which states contribute to the formation of the Kondo system and how the relative magnitudes of the Kondo temperatures can at least semi-quantitatively be understood [15, 16].

We present here results obtained by low temperature STM and STS concentrating on understanding which states at the metal surface play a major role in forming the Kondo ground state and how trends of the Kondo temperature can be understood when comparing different adsorption geometries of the adsorbate on a specific host material. In Sect. 3 we study the interaction of the surface-state electrons with the magnetic impurity by measuring the scattering phase shift. In Sect. 4 we discuss the behavior of T_K when the number of nearest neighbors around the adatom is changed.

2 Experimental

Single crystal surfaces were prepared by standard sputtering and annealing cycles in ultra-high vacuum (base pressure 1×10^{-10} mbar). The samples were then transferred in situ to an STM working at 6 K. Co adatoms were produced by dosing Co from a carefully out-gassed tungsten wire with a Co wire of 99.99% purity wrapped around it. During that process the sample temperature stayed below 20 K ensuring the formation of single adatoms due to a repulsive interaction between them on noble metal (111) surfaces [17]. Spectroscopic measurements were performed using a lock-in technique with a modulation of the sample voltage of 1 mV_{RMS} at a frequency of 4.5 kHz. All bias voltages are sample potentials measured with respect to the tip.

3 Kondo effect and resonant scattering: interaction with surface-state electrons

The first STS experiments with Kondo impurities were all carried out on noble metal (111) surfaces. These surfaces exhibit a surface state at E_F situated inside a band gap occurring in the [111] direction of the bulk crystal. The surface states are very attractive for investigations by STM since they are to some degree decoupled from the bulk states and have considerable amplitude at the tip position in vacuum above the surface. Furthermore, the surface-state electron density can be modified laterally by defects like steps or

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5 Conclusions

We have presented STM and STS measurements of the properties of the Kondo many-electron state formed by Co adatoms on noble metal surfaces. Notwithstanding the large weight of the surface-state electrons at the surface and in the vacuum above the surface, we show that for the case Co on Ag(111) the surface state does not determine the measured resonant line shape. To this end we measured the scattering phase shift the surface-state electrons acquire when scattering off the fully spin-screened Co impurity. We argue that the reason for the low contribution towards the line shape lies in the small effective coupling of the Co d -levels to the surface-state electrons. This low coupling also explains why the Kondo temperature is neither influenced by details of the surface-state properties nor by the density modulations present near e.g., steps on the (111) surfaces. For Co impurities on copper surfaces we have shown that T_K increases with increasing number of nearest neighbors. Experimentally the measurements were taken on the Cu(111) and Cu(100) surface (three, respectively, four nearest neighbors) and at a step edge on Cu(111) (5 neighbors). We explain the increase in T_K by an increase of hybridization of the magnetic impurity with the bulk electronic system of the crystal. This establishes the general trend and should serve as a basis for a theoretical treatment of the hybridization of Co on surfaces involving all electronic states present. Such a treatment is still needed to e.g. explain the relation between the Kondo temperature of Co adsorbed on Cu compared to that of Co on Ag or Au.

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Magnetism and structure on the atomic scale: Small cobalt clusters in Cu(001)Š. Pick,¹ V. S. Stepanyuk,^{2,*} A. L. Klavsyuk,³ L. Niebergall,² W. Hergert,³ J. Kirschner,² and P. Bruno²¹*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic*²*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*³*Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany*

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The interplay between structure and magnetic properties of small cobalt clusters embedded in a Cu(001) surface is studied performing *ab initio* and tight-binding calculations in a fully relaxed geometry. We reveal that, despite the small macroscopic mismatch between Co and Cu, the strain relaxations at the interface have a profound effect on the structure of the clusters and the substrate. The physical mechanism responsible for the strain relaxations in embedded clusters is related to the size-dependent mesoscopic mismatch which has been recently introduced to understand homo- and heteroepitaxial growth at the mesoscale [O. V. Lysenko *et al.*, Phys. Rev. Lett. **89**, 126102 (2002)]. We show that the atomic relaxations strongly reduce the magnetic anisotropy energy (MAE) and the orbital magnetic moments of embedded clusters. The largest MAE of about 1.8 meV is found for a single Co atom in the Cu(001) surface. A strong enhancement of the spin magnetic moments in embedded clusters as compared to a single atom of Co incorporated in the Cu(001) surface is found. Magnetic properties of embedded and supported clusters are compared. While in supported clusters the MAE is strongly enhanced at the edge atoms, the immersion of the cluster into the surface and atomic relaxations make the distribution of the local MAE contributions and orbital-moment values almost homogeneous.

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I. INTRODUCTION

Recent remarkable experiments on small magnetic clusters on metal surfaces have opened up unprecedented opportunities for atomic engineering of new magnetic materials.¹⁻⁶ By increasing the cluster size in an atom-by-atom fashion, Gambardella *et al.*¹ have studied how the magnetization and the magnetic anisotropy energy (MAE) develop in cobalt nanoparticles on Pt(111). They have reported the MAE of 9 meV for single cobalt adatoms, which is about 200 times larger than that of cobalt atoms in a bulk crystal. The larger the MAE, the more stable is the magnet. These results suggest that only a few hundred atoms would be needed to make a stable magnetic bit. Experiments of the group of Crommie² have raised the possibility to study the Kondo effect in small clusters and interactions between magnetic adatoms. Very recently the superlattice of magnetic adatoms has been created by Schneider *et al.*³ by exploiting the surface-state mediated long-range adsorbate interactions.⁶ Rusponi *et al.*⁴ have revealed that the MAE in supported clusters is nearly exclusively caused by the edge atoms alone. This finding opens new possibilities to tune the magnetic anisotropy and moment of nanostructures. The central role that have the edge cluster atoms in the MAE indicates that it could be possible to reduce the cluster size without running into the superparamagnetic limit and to use small clusters for single-bit magnetic data storage. The existence of both short- and long-range ferromagnetic order for finite monoatomic cobalt chains on a Pt substrate was reported by Gambardella *et al.*⁵ It has been found that by decreasing the coordination of the magnetic atoms, values of the MAE are obtained that are two orders of magnitude larger than those in bulk. These results confirm the theoretical prediction of Dorantes-Dávila and

Pastor about a strong enhancement of the MAE in the 3d transition-metal chains.⁷ The first calculations for adatoms and small clusters on metal surfaces⁸⁻¹⁰ have found very large orbital moments and MAE.

The above mentioned experiments require low operating temperature down to several tens of Kelvins or even lower. With increasing temperature adatoms and small clusters would become unstable due to the thermally enhanced surface diffusion and the interfacial intermixing may take place. Atomic exchange processes for single adatoms and burrowing of clusters into the substrate have been reported in several experiments and calculations even for metals immiscible in the bulk.¹¹⁻¹³ Experiments of Kurnosikov *et al.*¹⁴ have shown that it is possible to manipulate single atoms of Co embedded into a Cu(001) surface with scanning tunneling microscopy (STM) tip and to create in a controlled way small clusters which are stable at room temperature. In very recent scanning tunneling spectroscopy (STS) studies of Quaa *et al.*,¹⁵ the Kondo resonance was revealed on single Co atoms embedded in the Cu(111) substrate. The Kondo temperature was reported to be about 400 K which is significantly higher than for Co adatoms.¹⁶ We believe that the above experiments will undoubtedly stimulate experimental and theoretical studies of small clusters in subsurface layers. To the best of our knowledge there have been only a few calculations of magnetic properties of surface embedded clusters. For example, Klautau and Frota-Pessôa¹⁷ have performed an *ab initio* study of spin magnetic moments of non-relaxed Co agglomerates of different sizes and shapes embedded in Cu(001). They have found that the variation of the local moments in the clusters is mainly governed by the position of the site relative to the surface and the number of Cu neighbors. *Ab initio* calculations¹⁸ have demonstrated that

have a strong effect on the magnetic properties at the interface. The size-dependent mesoscopic mismatch is the driving force of the strain relaxations in the island and the substrate. We have shown that the MAE of the embedded clusters is significantly reduced compared to those in supported clusters. The interaction with the substrate atoms and the atomic relaxations drastically reduce the MAE of edge atoms of embedded clusters which play a major role for supported clusters. Atomic relaxations are also found to reduce the orbital magnetic moments of embedded clusters. For all clusters, including a single Co atom, in-plane magnetization is energetically preferred over the perpendicular one. We have found a strong enhancement of the spin magnetic moments in embedded Co clusters compared to a single Co atom in the Cu(001) surface. We believe that our results are of fundamental value to understand how the magnetic properties of nanostructures change due to the interface intermixing. We have used for our studies a particular system, Co islands in the Cu(001) surface, which has been believed not to exhibit a

strong strain relaxation. However, our results clearly demonstrate that due to the mesoscopic mismatch, strain relaxations and their impact on magnetic properties could be stronger than expected. It would be of great interest to study the effect of mesoscopic relaxations on magnetic properties for a system having a large macroscopic mismatch, for example Fe islands on W or Pd substrates. We expect that in such cases the impact of relaxations on magnetism can be crucial. Such studies are in progress now.

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Magnetic nanostructures stabilized by surface-state electrons

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Performing state of the art *ab initio* studies, we predict that new 3d magnetic nanostructures and superlattices on Cu(111) can be stabilized by surface-state electrons. We reveal that magnetic states in these systems are determined by long-range exchange interaction between adatoms. Atomic scale simulations indicate that 3d superlattices on Cu(111) can be stable up to 25–30 K.

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In recent years there has been a strong interest in the physics of magnetic nanostructures deposited on metal surfaces.^{1,2} It is believed that such structures can be of great importance for the development of advanced atomic scale magnetic devices. The control and manipulation of magnetism and structure on the atomic scale is an ongoing challenge of materials science.

Very recently a method in atomic engineering was demonstrated by a group headed by W.-D. Schneider.³ They have shown that cerium adatoms, deposited on Ag(111), can self-assemble into large ordered superlattice. These remarkable experiments raise the possibility for achieving new magnetic structures on metal surfaces.

The key idea of the experiment of Silly *et al.*³ is connected to long-range adsorbate interaction mediated by surface-state electrons. The quantum interference between the electron wave traveling towards the scattering defect, for example to an adatom, and the backscattered one leads to standing waves in the electronic local density of states (Fig. 1) and to Friedel-type indirect adsorbate-adsorbate interaction.⁴ Recently, low-temperature scanning tunnel microscope (STM) experiments^{5,6} and *ab initio* studies^{7–9} have resolved substrate-mediated interactions between adatoms. At short distances, the indirect electronic interactions are dominated by a rapidly decaying repulsive part (see Fig. 1). If the thermal energy of adatoms is not sufficient to overcome the repulsive barrier A, the dimers are not formed. In this case, as it was proposed by Knorr *et al.*⁶ and proved by experiments of Silly *et al.*,³ a hexagonal superlattice with the first nearest-neighbor (NN) adatom position corresponding to the first minimum of the interaction energy can be formed.

In this paper, performing state of the art *ab initio* studies, we predict that new magnetic nanostructures and superlattices on Cu(111) can be stabilized by the surface-state electrons. Adatom bonding in these structures is determined by a long-range interaction between adatoms. We reveal that spin-spin correlations at large adatom-adatom separations are caused by surface-state electrons. Our study demonstrates that magnetic states in nanostructures stabilized by surface-state electrons are dominated by an indirect exchange interaction between the magnetic adatoms. Atomic scale simulations show that magnetic superlattices on Cu(111) can be stable up to 25–30 K.

Our *ab initio* studies are based on density-functional theory in the local spin density approximation (LSDA) and the multiple-scattering approach in the framework of the Korringa-Kohn-Rostoker (KKR) Green's function method for adatoms and supported clusters.^{9–11} For short and intermediate distances, fully self-consistent total energy calculations are performed to find the interaction energies. However, for large adatom-adatom separations we calculate the interaction energy using the single-particle energies alone, as was proposed by Hyldgaard and Persson.¹² Our studies have shown that such an approach is well justified due to the screening of the Coulomb potentials of adatoms by the substrate electrons. The details of our approach have been given in our previous publications.^{9–11,13}

We have performed calculations for the interaction energy between 3d adatoms on Cu(111) for adatom-adatom separations up to 50 Å. In all cases we have found that the interaction energy is oscillatory with a period of $\lambda_F/2 = 15$ Å [λ_F is a surface-state Fermi wavelength of Cu(111)] and has the repulsive barrier A (cf. Fig. 1).¹⁴ The first minimum is found to be about 12 Å for all 3d pairs. The repulsive barrier B at 19 Å is considerably smaller than barrier A. Therefore, the

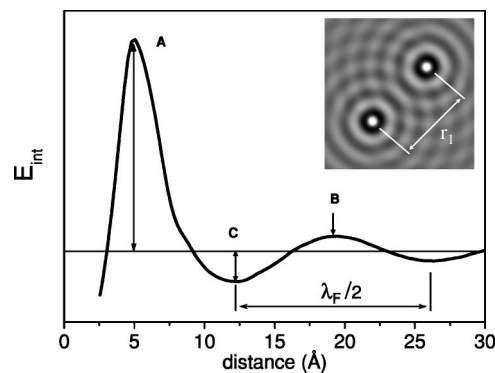


FIG. 1. Schematic description of the interaction energy between adatoms. Such form of the interaction energy has been found in *ab initio* calculations for all 3d pairs. Repulsive barriers A and B, and the depth of the potential C for all 3d pairs are presented in Table I. The inset shows, as an example, standing waves of the local density of states (LDOS) between the two Co adatoms separated by a distance r_1 equal to the minimum of the potential C.

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