# Correlated Electrons Step by Step: Itinerant-to-Localized Transition of Fe Impurities in Free-Electron Metal Hosts

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High-resolution photoemission spectroscopy and *ab initio* calculations have been employed to analyze the onset and progression of $d$-$sp$ hybridization in Fe impurities deposited on alkali metal films. The interplay between delocalization, mediated by the free-electron environment, and Coulomb interaction among $d$ electrons gives rise to complex electronic configurations. The multiplet structure of a single Fe atom evolves and gradually dissolves into a quasiparticle peak near the Fermi level with increasing host electron density. The effective multiorbital impurity problem within the exact diagonalization scheme describes the whole range of hybridizations.

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Electronic states in solids exhibit either itinerant or localized behavior depending on a number of factors, such as the type and strength of chemical bonding, local atomic arrangement and dimensionality of the system. This duality represents a long-standing challenge in solid state physics, barring a general theory of electron transport and magnetic phenomena, as well as in other areas of science including astrophysics [1]. The standard band theory based on the Bloch theorem [2] describes very well many properties of metals and semiconductors, which can be generally explained by Landau's Fermi-liquid theory with its postulate of a one-to-one correspondence between states of bare particles and quasiparticles [3]. At the same time, electron states in atoms are classified in terms of *many-particle* quantum numbers of total spin ($S$), orbital ($L$) and total angular ($J$) momentum forming a multiplet structure. It is intuitively clear that in some cases this description should survive in solids as well, assuming that an overlap of atomic states is small enough. There is, however, no simple way of relating the many-electron atomic states with the single-particle Bloch waves.

The established theory of atomic multiplet structure describes with great accuracy the complex spectra of transition-metal ions [4]. The main mechanism of energy level formation in this case is related to the strong Coulomb interaction among $3d$-electrons. The factor determining whether an atomic multiplet structure should form, or if energy bands are to be expected, is the competition between the Coulomb energy and the kinetic energy associated with electrons hopping from site to site in the lattice. When neither of these two terms dominates, one often observes complicated electron states that are manifestations of electron correlation. Electronic correlation is a crucial ingredient not only in the narrow $d$-band systems, but also in rare-earth [5], actinide [6], and even some $sp$ compounds, like the superconducting fullerene family [7].

Narrow quasilocalized $d$ states play an important role in the electronic structure of low-dimensional transition-metal systems, including surfaces and nanoparticles. When nanosized materials approach the atomic limit one may hence expect that conventional theoretical models fail, and the question is how to describe these systems appropriately. For instance, the magnetic moments of single Co atoms on a Pt surface cannot be reproduced using conventional theoretical methods, which ignore electron correlations [8]. Indeed, the case of individual magnetic impurities is highly nontrivial and may be considered as a benchmark for understanding electron correlation in $d$-metal systems. For moderate hybridization between impurity and host electron states the Anderson model describes well the formation of a magnetic moment and the many-body spin-flip processes that lead to the Kondo effect [9]. However, for rare-earth impurities one should start with the multiplet structure of a free atom and then introduce hybridization effects as a perturbation [10]. These two approaches are closely related with the limiting cases of "strong" and "weak" hybridization, whereas a generic intermediate case, schematized in Fig. 1, seems to be very difficult to understand.

Direct spectroscopic methods can be used to probe in detail the transition from an atomiclike multiplet structure to a band energy spectrum. Nevertheless, no experimental or theoretical study has shown how the transition occurs between atomiclike and itinerant electron configurations, when the relative importance between electron hopping and Coulomb repulsion is carefully tuned. The experimental verification of multiplet-to-band transitions is a delicate task that requires appropriate choice of a $d$ metal and conduction electron "bath" systems. Here we focus on Fe impurities bound to different alkali surfaces, which represent a realistic approximation to a free-electron metal and whose charge density can be varied stepwise by moving along the alkali group in the periodic table [2].

Dilute Fe impurities were deposited by $e$-beam evaporation on multilayer alkali metal films condensed on single-crystal Cu(100) in ultrahigh vacuum. To avoid aggregation, minute amounts of Fe atoms were deposited and measured at 20 K, below the onset of thermal diffusion. The Fe surface concentration is indicated as a fraction of a monolayer (1 ML $= 1.6 \times 10^{15}$ atoms cm$^{-2}$ ). Scanning tunneling microscopy (STM) was performed before and after deposition of ~0.01 ML Fe on K and Li layers, representative of alkali species with large and small atomic radius, respectively. In both cases, we observe that Fe adsorbs in the form of random isolated impurities on top of the exposed alkali surface. Figure 2(a) shows the surface topography after deposition of Fe impurities on Li/Cu(100) which appear as round protrusions of about 10 Å FWHM. STM conductance spectra of Fe on Li reveal an electronic resonance centered about the Fermi level ($E_F$) that is the signature of a many-body Kondo state [11,12] with characteristic temperature $T_K = 96$ K [Fig. 2(c)]. As shown in Fig. 2(b), such a spectral feature can be used to univocally identify the Fe adatom position.

Photoemission electron spectroscopy experiments were performed at the ID4 and PGM 56 beam lines of the Elettra and BESSY synchrotron radiation facilities to measure the valence band electron configuration of the Fe. Photoemission spectra were recorded using 50–120 eV photon energy in normal emission with 8° angular acceptance and 15 meV energy resolution. Figure 3 shows the photoemission spectra of dilute Fe impurities on a K film as a function of Fe coverage recorded with photon energy $h\nu = 120$ eV. The spectral features of the Fe $3d$ states can be clearly detected even at very low atomic concentrations owing to the favorable cross section ratio with respect to the alkali $sp$ states [13]. The Fe spectra display clear signatures of multiplet structures around $-3$ and $-0.3$ eV below $E_F$, whose line shape and position, after subtraction of the substrate emission, is unchanged up to the impurity coalescence threshold of about 0.035 ML. In agreement with a core level x-ray absorption study of Fe impurities on K [14], these features are assigned to a nearly atomiclike Fe $d^7$ configuration, representing strongly localized high spin and low spin terms superposed to the $sp$ substrate bands.

Depending on the atomic volume of the alkali ions, the surface electron density can be decreased or increased by moving towards heavier and lighter alkali species, respectively. We find the hybridization of the Fe $d$ states to change drastically from being very weak for Cs to much stronger for Li. Figure 4 shows photoemission spectra for 0.01 ML Fe atoms on Cs, K, Na, and Li hosts after subtraction of the surface background. From Cs to K only a reduction of intensity of the multiplet features is observed accompanied by a moderate energy broadening. On Na and Li, however, the spectra change *qualitatively*, indicating the onset and progression of $d$-$sp$ electron hybridization. For Fe on Li the spectrum presents a renormalized quasiparticle resonance near $E_F$ and lower Hubbard bands

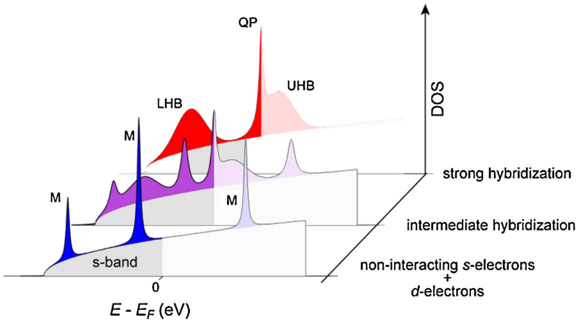

FIG. 1 (color online). Spectral function of a many-body $d$-electron impurity and host conduction electrons: localized impurity limit (bottom); intermediate coupling (middle); strong hybridization limit (top). Letters indicate multiplet (M), quasiparticle resonance (QP), lower and upper Hubbard bands (LHB, UHB) spectral features.

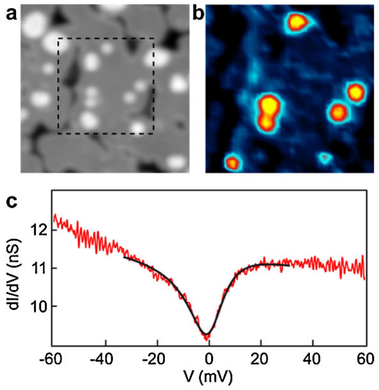

FIG. 2 (color online). (a) Constant current STM image of Fe impurities deposited on ~3.8 ML Li/Cu(100). Fe adatoms appear as small round protrusions; larger dots represent Li islands growing on the topmost percolated Li layer. Image size $177 \times 177$ Å$^2$, the linear gray scale goes from 0 to 5 Å. (b) $d^2I/dV^2$ map of the dashed region in (a) showing spatially-resolved Kondo resonances corresponding to individual Fe impurities (set point $V = 7$ mV, $I = 0.1$ nA). (c) $dI/dV$ spectrum measured on top of a Fe adatom (set point $V = -100$ mV, $I = 0.5$ nA). The thick solid line is a fit to the data according to Ref. [12]. Images and spectra were recorded at 5 K.

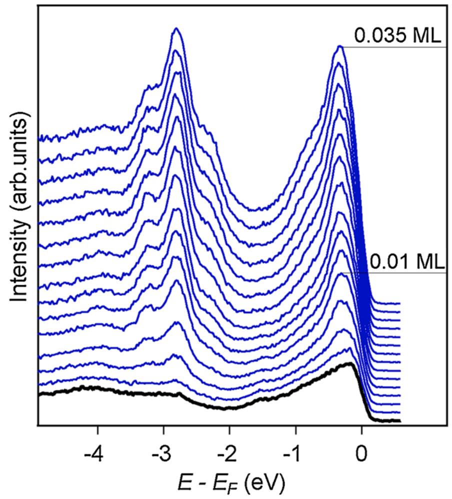

FIG. 3 (color online). Photoemission spectra of Fe impurities on a K film. The bottom spectrum represents the substrate photoemission background. The intensity of the Fe-induced spectral features increases with Fe coverage from bottom to top. No changes in the spectral line shape are observed in the isolated impurity limit below 0.035 ML.

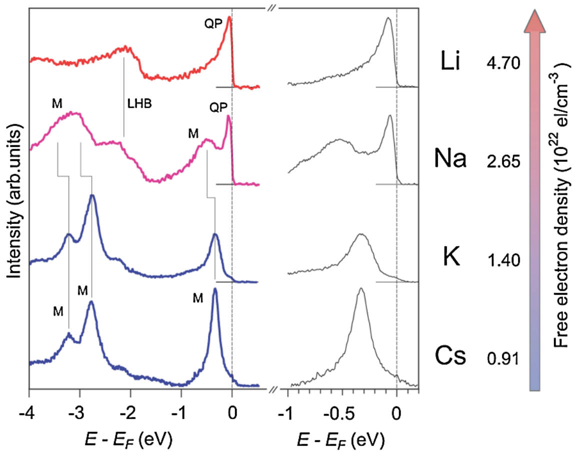

FIG. 4 (color online). Host-dependent Fe impurity photoemission spectra and free-electron density (from Ref. [2]). The data represent the impurity photoemission intensity after subtraction of the alkali background (see Fig. 2).

around $-2$ eV. In the Anderson model, the quasiparticle resonance peak near $E_F$ is identified with the Kondo effect, representing low-energy excitations that involve the spin degrees of freedom of the impurity and conduction electrons, in accord with the STM data. Remarkably, compared to previous studies [11,12,15], this is the first time that both Hubbard and Kondo correlation fingerprints are observed in a metal impurity system, which we find reminiscent of a strongly correlated solid, e.g., $V_2O_3$ [16,17]. Moreover, a most interesting and totally unique feature is found for the Fe-Na system: the photoemission spectrum in this case is a mixture of an atomic multiplet structure, quasiparticle bands near the Fermi level, and the low lying Hubbard bands around $-2$ eV. Such features, indicated by labels in Fig. 4 and later exemplified by our theoretical analysis, mark the transition between the localized and hybridized extremes of Fig. 1.

These data provide a model system to test general *ab initio* theories of localized-to-itinerant electron behavior. In order to do so, one needs to incorporate both many-body effects from the strong local Coulomb interaction among $d$ electrons with hybridization effects due to the surrounding electronic bath of the host. All these many-body effects are beyond traditional electronic structure calculations; however, the recently developed first-principles dynamical mean field theory (DMFT) [16–18] brings the prospect of investigating electronic correlations in realistic complex systems, studying the crossover from atomiclike behavior to bandlike spectral properties.

To analyze the experimental results we have calculated the electronic structure of the Fe impurities in a bath of alkali electronic states using different impurity solvers of the DMFT method [16]. In this approach, the original many-body problem of the crystal is split into a *one-electron* problem for the lattice with a self-consistent local self-energy and a many-body *single-site* problem for a quantum impurity in an effective medium. We used the density functional method for estimating the electronic structure of different alkali crystals. A complete four-index intra-atomic Coulomb interaction matrix $U_{ijkl}$ is taken into account, with an average Hubbard parameter $U = 8$ eV and an exchange parameter $J = 0.85$ eV, which correspond to the optimal choice for the screened Coulomb interactions for Fe [16]. The corresponding impurity problem can be described by the following multiorbital Anderson impurity model:

$$H_{\text{imp}} = \sum_{ij\sigma} \varepsilon^d_{ij} d^+_{i\sigma} d_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} U_{ijkl} d^+_{i\sigma} d^+_{j\sigma'} d_{l\sigma'} d_{k\sigma} + \sum_{ik\sigma} (V_{ik} d^+_{i\sigma} b_{k\sigma} + V_{ki} b^+_{k\sigma} d_{i\sigma}) + \sum_{k\sigma} \varepsilon^b_k b^+_{k\sigma} b_{k\sigma}, \tag{1}$$

where $d^+$, $d$ and $b^+$, $b$ are creation and annihilation operators for correlated $d$- and bath $sp$-electrons, respectively, $\varepsilon^d$ and $\varepsilon^b$ are the one-electron energies of correlated and bath electrons, and $V_{ik}$ is the hybridization matrix. Starting from density functional calculations of one-electron matrix elements of the effective Anderson Hamiltonian, we performed many-body calculations using different approximations. The most accurate scheme corresponds to the continuous time quantum Monte Carlo solutions of the impurity Hamiltonian. In this method, the resulting Green function obtained in imaginary time should be analytically continued to the real energy axis, with the effect that all multiplet structures disappear [19]. We also found that the simple Hubbard-I approximation [20] overestimates the tendency towards multiplet formation and hence it cannot explain the quasiparticle formation in the Fe-Li system. Finally, the most successful approach

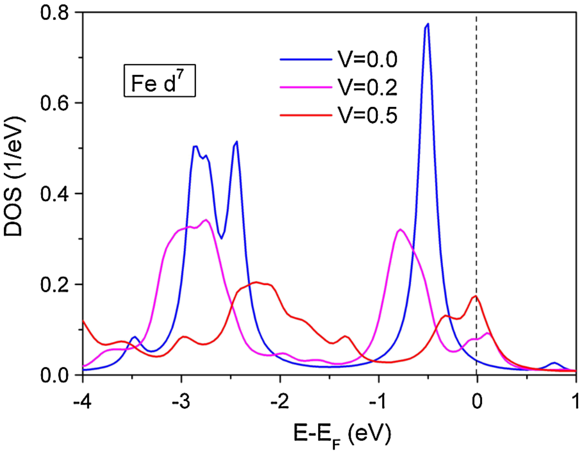

FIG. 5 (color online). Theoretical spectral function of Fe impurities in alkali metal hosts. Colors refer to the electron conduction bath with zero (blue: $V = 0$ eV), small (purple: $V = 0.2$ eV) and large (red $V = 0.5$ eV) hybridization. The general Coulomb vertex is defined through the Slater parameters $F^0 = 8$ eV, $F^2 = 7$ eV, and $F^4 = 5$ eV, corresponding to $U = 8$ eV and $J = 0.85$ eV.

to describe the transition from atomic multiplet structures to a broad energy band is obtained with the exact diagonalization scheme for the solution of the impurity problem. We find that already a small number of orbitals in the fermionic bath is sufficient to change drastically the multiplet structure.

In Fig. 5 we show how the quasiparticle spectral function evolves as a function of the hybridization strength, $V$, using a single bath orbital. The average hybridization strength has been estimated to be about 0.5 eV for the Fe-Li system, 0.2 eV for Fe-Na, and very small for Fe-Cs and Fe-K, by means of fully relaxed VASP calculations of an Fe impurity adsorbed on a 7-layer bcc alkali slab. The negligibly weak hybridization ($V \sim 0$ eV) reproduces the $d^7$ multiplet structure of the Fe-Cs and Fe-K systems with good accuracy. The small hybridization with the fermionic bath ($V \sim 0.2$ eV) corresponds to the intermediate Fe-Na system with a combination of atomic multiplets and quasiparticle states at $E_F$, together with the new low Hubbard bands around $-2$ eV. Note that, in accordance with the experiment, the Hubbard band and multiplet states broaden and shift to higher binding energy as the spectral weight is redistributed towards the quasiparticle resonance at $E_F$. We speculate that a possible reason for the formation of a "mixed multiplet-band" feature is related to an anisotropic hybridization function. In theoretical calculations only a fully symmetric combination of Fe $d$ orbitals can hybridize with an $s$-like bath orbital. In the experimental situation such anisotropy can occur due to anisotropic hopping matrix elements between the Fe impurity and alkali metal surface atoms, which often have a complicated structure. Finally, the large hybridization with the fermionic bath ($V \sim 0.5$ eV) corresponds to the Fe-Li system, where the atomic multiplet structure is removed and only the correlated quasiparticle peak and broad Hubbard bands around $-2$ eV are formed. Accurate description of the Kondo resonance at the Fermi level is beyond our crude discretization of the hybridization function and can be obtained in the quantum Monte Carlo scheme [19]. There is still an important question about the nonlocal effects related with effective $d$-$d$ interactions in these systems. We believe that for such small iron concentration impurity effects play the dominant role in the formation of the spectral function.

In conclusion, photoemission measurements of Fe impurities on alkali metal surfaces clearly show the effect of how atomic multiplets develop in solids when the relative strength of Coulomb repulsion and band formation effects are carefully balanced. The nice agreement between the experimental photoemission spectra, STM, and exact diagonalization impurity scheme proves the importance of considering full electron correlation effects as well as anomalies of the hybridization function in the interpretation of energy bands in transition-metal systems.

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