Origin of the giant magnetic moments of Fe impurities on and in Cs films

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To explore the origin of the observed giant magnetic moments ($\sim 7\mu_B$) of Fe impurities on the surface and in the bulk of Cs films, we have performed the relativistic LSDA + $U$ calculations using the linearized muffin-tin orbital (LMTO) band method. We have found that Fe impurities in Cs behave differently from those in noble metals or in Pd. Whereas the induced spin polarization of Cs atoms is negligible, the Fe ion itself is found to be the source of the giant magnetic moment. The 3$d$ electrons of Fe in Cs are localized as the 4$f$ electrons in rare-earth ions so that the orbital magnetic moment becomes as large as the spin magnetic moment. The calculated total magnetic moment of $M = 6.43\mu_B$, which comes mainly from Fe ion, is close to the experimentally observed value.

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The problem of magnetic impurities in metals has been an important branch of solid state physics [1]. The Anderson impurity Hamiltonian or the Kondo impurity Hamiltonian has been a starting point of the model calculations. In the side of electronic structure calculation, it is difficult to apply the local spin density approximation (LSDA) [2] in its original form, because the Coulomb correlation energy of 3$d$ electrons is underestimated in the LSDA.

Recently, giant magnetic moments are observed in the anomalous Hall effect measurements for the Fe and Co transition element, and so Pd atoms nearby magnetic Fe impurities in Pd films [4]. Pd is a near-magnetic metal, and so Pd atoms nearby magnetic Fe impurity are easily spin polarized to yield giant magnetic moments. Whether this is also true for Fe impurities on Cs films is a question to be addressed in this work.

The magnetic moments of 3$d$ transition metal elements in solids are usually determined by the spin magnetic moments. The orbital magnetic moments are quenched by the crystal field and/or the hybridization effects. In contrast, 4$f$ rare-earth elements have comparable sizes of the orbital magnetic moments to those of the spin magnetic moments. The total magnetic moment $M$ is given by $M = g_d\mu_B [J(J + 1)]^{1/2}$, where $J$ is the total angular momentum determined by the Hund’s rule: $J = |L - S|$ (L + S) for $n \leq (2l + 1)$ ($n \geq (2l + 1)$), and $g_d$ is the Landé’s $g$-factor. According to the formula, a free Fe ion in an electron configuration of Fe$^{2+}$ will have effectively $M = 6.70\mu_B$, unless the orbital magnetic moment is quenched [3]. This theoretical magnetic moment is very close to the experimentally observed $M = 7\mu_B$ of Fe impurities in Cs [6]. Therefore, if Fe ions in Cs are isolated because of the large lattice constant of Cs metal, the main contribution to the observed magnetic moments will come from Fe ions themselves rather than from the induced spin polarization of the surrounding Cs atoms. In fact, previous local susceptibility data of Fe ions in heavy alkali-metals have been discussed in line with isolated 3$d$ states for Fe ions [4][7]. The present works are to determine what is realized in these systems.

We have simulated Fe impurities in Cs films using the linearized muffin-tin orbital (LMTO) band method [3]. In our calculations, we assume that Fe impurities are substitutional and the ideal body-centered-cubic (bcc) structure of Cs ($a = 6.05$ Å) is maintained even after impurities are introduced. Although the assumptions of the substitutional Fe impurities and the rigid lattice are not valid a priori, these effects are thought to be not so critical [2][4]. The function of the basis set is adopted up to $l = 2$ orbitals for all the atomic sites.

Since the Coulomb correlation interaction of Fe 3$d$ electrons is expected to be significant in these systems, the LSDA + $U$ method will be useful. The LSDA + $U$ [11] removes the deficiency of the LSDA by incorporating the Hubbard-like interaction term for 3$d$ electrons. Formally, the LSDA + $U$ Hamiltonian is given by

$$\mathcal{H}_{\text{LSDA} + U} = \mathcal{H}_{\text{LSDA}} - \left[ \frac{1}{2} UN(N - 1) - \frac{1}{2} J \sum_{\sigma} N_{\sigma}(N_{\sigma} - 1) \right]$$
$$+ \frac{1}{2} \sum_{(m),\sigma} V(m;m''m''')n_{m\sigma}^\sigma n_{m'm''\sigma}^{-\sigma}$$
$$+ \frac{1}{2} \sum_{(m),\sigma} [V(m;m;m'') - V(m';m''m''')]$$
$$\times n_{m\sigma}^\sigma n_{m'm''\sigma}^{-\sigma}$$

where $n_{mm'}^\sigma$ is the $d$ occupation number matrix of spin $\sigma$, $F^k$ is the Slater integral, and $c^\dagger(l,m : l,m')$ is a Gaunt coefficient. The conventional notations, $N_{\sigma} = \sum_m n_{mm}^\sigma$ and $N = \sum_{\sigma} N_{\sigma}$, are used. Two main parameters in the LSDA + $U$ are the Coulomb $U$ and the exchange $J$ interactions. These parameters are related to the Slater interactions.
FIG. 1. The LSDA DOS of 1Fe/5Cs ML structure. Fe 3d-bands are extremely localized and the shape of Fe 4s DOS exhibit a typical 2D DOS. The spin polarization of Cs 6s-bands is due to the hybridization with Fe bands. The spin magnetic moment of the first NN Cs is very small, $-0.09 \mu_B$.

To determine the size of orbital magnetic moments, we have explicitly included the spin-orbit coupling in the Hamiltonian [14]. In this way, our calculational scheme corresponds to a fully relativistic LSDA + U method. We have used 80 k-points sampling for the tetrahedron integration in the irreducible Brillouin zone wedge, except for 40 k-points sampling in the LSDA + U calculation for a supercell.

First, we have considered multilayered (ML) structures of Fe and Cs, which are stacks of the conventional bcc unit cells along the [001] direction. For 1Fe/3Cs structure which contains a monolayer of Fe after three layers of Cs, the magnetic ordering is tested by the LSDA total energy calculations. The antiferromagnetic state is lower by only about 1 mRy than the ferromagnetic state. This result, however, is within the limit of the numerical precision, and thus one cannot ascertain which state is the ground state. Indeed, the experiment [3] identifies the local magnetic moment formation, but the existence of the long range order is not confirmed. Other experimental tools are required to reveal the long range order in the system. In the following discussion, we will consider only the ferromagnetic ordering state.

Figure 1 is the LSDA density of states (DOS) at each atomic site for 1Fe/5Cs ML structure. The Fe-Fe bond lengths are $a = 6.05 \, \text{Å}$ in plane and $3a = 18.15 \, \text{Å}$ out of plane. The spin-up bands of Fe 3d is at about $-2.8 \, \text{eV}$ below the Fermi level $E_F$. In fact, it is more appropriate to call Fe 3d-levels rather than 3d-bands. The energy levels are well-defined outside of Fe 4s- and Cs 6s-bands so that the spin-up electrons of Fe 3d do not hybridize with other electrons and form local levels. On the other hand, the spin-down bands of Fe 3d are slightly mixed with Cs 6s-bands at $E_F$ and show an energy dispersion. Interestingly, the shape of Fe 4s-bands is reminiscent of a typical 2-dimensional (2D) DOS which has a logarithmic divergence in the band center and becomes constant at the band edges. We have also found similar features for
Fe ions in 1Fe/3Cs ML. This suggests that the Fe $s$-$s$ interaction rapidly diminishes over $2a = 12.10$ Å, despite the delocalized characteristics of $s$ electrons, and Fe ions are essentially isolated in the c-direction.

The spin splittings of Cs bands are seen for the first and the second nearest neighbor (NN) Cs of Fe, and it becomes negligible for the third NN Cs. The induced spin magnetic moments at Cs sites are $-0.09\mu_B$ and $-0.02\mu_B$ for the first and the second NN, respectively. The hybridization of Cs $6s$-bands with Fe bands, stronger in the minority band, populates the spin-down states of Cs $6s$ and drives the spin magnetic moments at Cs sites to align antiferromagnetically to the spin of Fe ion. The spin and the orbital magnetic moments of Fe ion are, respectively, $\mu_S = 3.46\mu_B$ and $\mu_L = 1.59\mu_B$ in the LSDA. When the LSDA $+$ $U$ is applied, they become $\mu_S = 3.12\mu_B$ and $\mu_L = 2.87\mu_B$. The Coulomb correlation effects is obvious, which enlarges the $3d$-level splitting and increases the orbital magnetic moment. The large orbital magnetic moment manifests that Fe $3d$ states are localized in Cs.

A comparison with the system of Fe impurities in Pd will be helpful to understand Fe in Cs. In Fig. 2, we show the LSDA DOS for 1Fe/5Pd ML structure, of which the stacking unit is the face-centered-cubic (fcc) unit cell of Pd. We show for Pd sites only the 4d DOS. The exchange splitting of Fe 3d-bands is still large $\sim 3$ eV, and the spin magnetic moment of Fe ion is $\mu_S = 3.12\mu_B$ in Pd, which are similar sizes to those of Fe in Cs. However, the orbital magnetic moment of Fe ion is negligible $\mu_L = 0.09\mu_B$ in Pd. The 3d orbitals of Fe are greatly deformed by the hybridization with Pd, and so Fe loses most of its ionic nature in Pd. This feature is very different from the case of Fe in Cs. The spin magnetic moments at the first and the second NN Pd sites are $0.30\mu_B$ and $0.07\mu_B$, respectively. Total sum of the spin magnetic moment of Fe and non-negligible spin magnetic moments of surrounding Pd atoms gives rise to the giant magnetic moment.

For a realistic simulation of Fe impurities in Cs films, we have constructed a supercell, the size of which is eight times larger than the bcc unit cell of Cs. The supercell has one Fe atom at the center and fifteen Cs atoms at the right sites. Considering that the Fe-Fe interaction becomes negligible over $2a = 12.10$ Å, the size of the supercell is large enough to examine Fe impurity effects. In the LSDA, the properties of Fe 3d-bands are not much different from those of ML structures. The spin-up bands of Fe 3d shift down a little bit to higher binding energy (see Fig. 3). In the LSDA $+$ $U$, notable differences are that Fe 3d states disappear near $E_F$ by the Coulomb correlation interaction, and the energy levels of Fe 3d are sharply split by the spin-orbit interaction in addition to the Coulomb correlation. Hence, the spin-down Fe 3d-bands no longer hybridize with Cs $6s$-bands. In the inset of Fig. 3, the angular distribution of the occupied Fe 3d spin-down states are plotted, based on the orbital dependent occupancies from the LSDA $+$ $U$ calculation. Although there is slight deviation from perfectly isolated states, the angular distribution is almost independent of the azimuthal angle rotation. The symmetric angular distribution indicates that Fe 3d states are well-localized in Cs. Besides the localization of Fe 3d electrons, the 2D shape of Fe $4s$-bands in the ML structure is destroyed and Fe 4s-bands become also localized in the supercell.

We summarize the calculated magnetic moments in Table II. Because of charge transfer from Cs sites, Fe ion gets about 0.5 (0.8) more electrons in the LSDA (LSDA $+$ $U$) and these electrons go to the minority bands of Fe 3d. While the transferred charge reduces the spin magnetic moment of Fe ion, the reduced spin magnetic moment is compensated by the enhanced orbital magnetic moment. The spin magnetic moments of Cs are antiparallel (parallel) to the Fe spin in the LSDA (LSDA $+$ $U$). The direction of the spin polarization in Cs atoms can be understood by the band hybridization effects. In the LSDA, the spin-down bands of Fe 3d hybridize with
Cs 6s-bands near $E_F$ populating the spin-down states of Cs 6s, whereas, in the LSDA + $U$, the occupied spin-down bands of Fe 3d are pushed down to about $-1.7$ eV below $E_F$ and remain as local levels. In the LSDA, the total magnetic moment of $M = 4.62 \mu_B$ is too small. It is because the spin-orbit coupling in the LSDA is not so effective to polarize orbitals. The correct orbital ordering is obtained only with the strong Coulomb correlation interaction. The total magnetic moment of $M = 6.43 \mu_B$ in the LSDA + $U$ is composed of Fe 94 % and Cs 6 % contributions. One can conclude from these results that the electronic states of Fe ion are almost fully localized in Cs, and the giant magnetic moment arises mainly from Fe ion itself rather than the induced spin polarization of Cs atoms. In this sense, 3d electrons of Fe in Cs should be treated as 4f electrons in rare-earth ions. It is desirable to check such a large orbital moment in this system with experimental tools such as the magnetic circular dichroism (MCD) or the resonant X-ray magnetic scattering. The small discrepancy from the experiment ($\sim 7 \mu_B$) may be due to improper use of $g_J = 2$ in the analysis, which counts only the spin contribution.

In addition to the giant magnetic moments of Fe impurities in Cs films, neither Fe coverage effects and nor moment change between Fe ions on the surface and in the bulk are observed. In general, magnetic impurities on the surface of solids have larger magnetic moments than in the bulk. On the surface, electrons are localized due to lack of the degree of freedom in the surface normal direction. These electrons, confined on the surface plane, results in enhanced magnetic moments. For Fe impurities in Cs films, Fe ions are fully localized even in the bulk, and thus further localization of Fe electrons does not occur on the surface. The negligible Fe coverage effects can be understood considering the short interaction range ($2a = 12.10$ Å) between Fe ions. The magnetic moment rarely depends upon the Fe concentration on the surface of Cs films, once excluding effects of the lattice relaxation and the rearrangement of surface atoms.

In conclusion, we have found that Fe impurities in Cs films have a different behavior from those in Pd films, and that the giant magnetic moments of Fe impurities in Cs originate mainly from the localized Fe ions but not from the spin polarizations of the neighboring Cs atoms. The contribution from the orbital magnetic moment of Fe 3d electrons is comparable to that from the spin magnetic moment, as in the 4f rare-earth ions. The Coulomb correlation interaction at the Fe site should be properly considered to get consistent results with experimental data.

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TABLE I. The calculated magnetic moments ($\mu_B$) for the supercell structure. The LSDA + SO represents a relativistic LSDA calculation. In the LSDA + $U$, we have explicitly included the spin-orbit interaction. The magnetic moments of Cs are sums of all the Cs moments in the supercell.

| Method       | total $M$ | Fe $\mu_S$ | Cs $\mu_S$ | Fe $\mu_L$ | Cs $\mu_L$ |
|--------------|-----------|-----------|-----------|-----------|-----------|
| LSDA         | 3.29      | 3.59      | -0.29     | 1.60      | -0.01     |
| LSDA + SO    | 4.62      | 3.54      | -0.51     | 1.60      | -0.01     |
| LSDA + $U$   | 6.43      | 3.14      | 0.42      | 2.90      | -0.04     |
|              |           |           |           |           |           |