

Origin of the Giant Magnetic Moments of Fe Impurities on and in Cs Films

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We have explored 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, using the relativistic local-spin-density-approximation 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 a source of the giant magnetic moment. The $3d$ electrons of Fe in Cs are localized as the $4f$ electrons in rare-earth ions so that the orbital magnetic moment becomes as large as the spin magnetic moment. The calculated total magnetic moment $M = 6.43\mu_B$ 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. 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) in its original form, because the Coulomb correlation energy of $3d$ electrons is underestimated in the LSDA.

Recently, giant magnetic moments are observed in the anomalous Hall effect measurements for the Fe and Co impurities on the surface and in the bulk of Cs films [1]. The deduced values of magnetic moments are $\sim 7\mu_B$ and $\sim 8\mu_B$ for Fe and Co impurities, respectively. These are unexpectedly large magnetic moments, as compared to $2.22\mu_B$ and $1.72\mu_B$ for pure Fe and Co metals. These features were explained in terms of induced spin polarization of the neighboring Cs atoms, as in the case of $3d$ magnetic impurities in Pd films [2]. Pd is a near-magnetic transition element, 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 in Cs films is a question to be addressed in this Letter.

The magnetic moments of $3d$ transition metal elements in solids are usually determined by the spin moments. The orbital moments are quenched by the crystal field and/or the hybridization effects. In contrast, $4f$ rare-earth elements have comparable sizes of the orbital moments to those of the spin moments. The total magnetic moment M is given by $M = g_J\mu_B[J(J+1)]^{1/2}$, where J is the

total angular momentum determined by the Hund's rule and g_J is the Landé's g factor. Accordingly, a free Fe ion in an electron configuration of Fe^{2+} will have an effective magnetic moment $M = 6.70\mu_B$ ($g_J = 3/2, J = 4$), unless the orbital moment is quenched [3]. This theoretical magnetic moment is very close to the experimentally observed $M \sim 7\mu_B$ of Fe impurities in Cs [1]. Therefore, if Fe ions in Cs are isolated somehow, 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 for Fe ions in heavy alkali metals have been discussed in line with isolated $3d$ states for Fe ions [4,5].

We have simulated Fe impurities in Cs films using the linearized muffin-tin orbital band method. In our calculations, we assume that Fe impurities are substitutional and the ideal body-centered-cubic (bcc) structure of Cs ($a = 6.05 \text{ \AA}$) 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 [6,7]. 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 $3d$ electrons is expected to be significant in these systems, the LSDA + U method will be useful. The LSDA + U [8] removes the deficiency of the LSDA by incorporating the Hubbard-like interaction term for $3d$ electrons. Formally, the LSDA + U Hamiltonian is given by

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

$$V(mm'; m''m''') = \sum_{k=0}^{2l} c^k(lm, lm'')c^k(lm''', lm')F^k, \quad (2)$$

where $n_{mm'}^\sigma$ is the d occupation number matrix of spin σ , F^k is the Slater integral, and $c^k(lm, lm')$ 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 integrals by $U = F^0$ and $J = (F^2 + F^4)/14$. The ratio of F^4/F^2 is known to be constant around 0.625 for most 3d transition metal atoms [9]. We have used parameter values of $U = 6.0$ eV and $J = 0.89$ eV [10].

To determine the size of orbital magnetic moments, we have explicitly included the spin-orbit coupling in the Hamiltonian [11]. In this way, our calculational scheme corresponds to a fully relativistic LSDA + U method. It has been shown that the LSDA + U method describes properly the orbital magnetism of solids with strongly correlated electrons [12]. 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 the 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 than the ferromagnetic state by only about 1 mRy. 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 [1] identifies the local magnetic moment formation, but the existence of the long range order is not verified. 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 the 1Fe/5Cs ML structure. The Fe-Fe bond lengths are $a = 6.05$ Å in plane and $3a = 18.15$ Å out of plane. The spin-up bands of Fe 3d are at about -2.8 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 two-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.

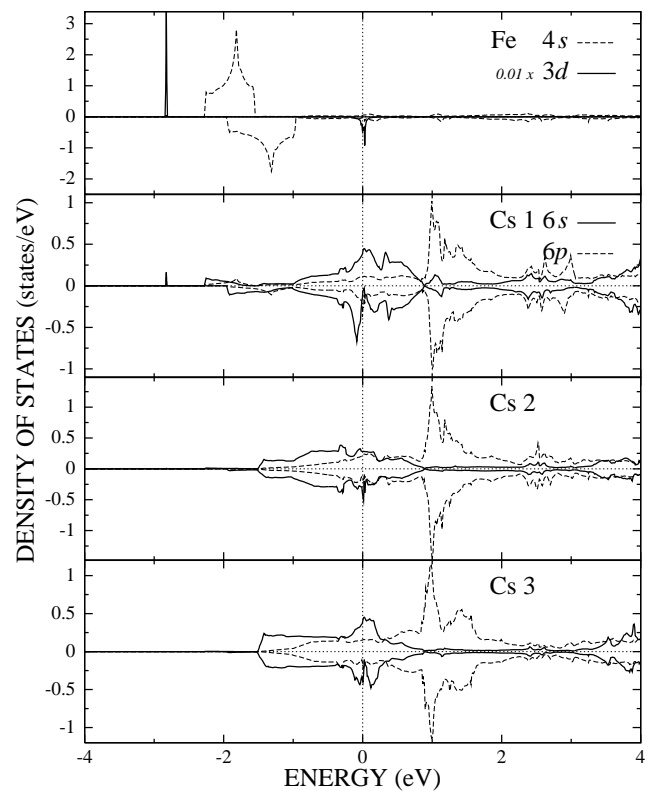


FIG. 1. The LSDA DOS of the 1Fe/5Cs ML structure. Fe 3d bands are extremely localized and the shape of Fe 4s DOS exhibit a typical 2D DOS. The spin polarization of Cs 6s bands is due to the hybridization with Fe bands. The spin magnetic moment of the first NN Cs is very small, $-0.09\mu_B$.

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 are obvious, which enlarges the 3d-level splitting and increases the orbital magnetic moment. Such large orbital magnetic moment indicates that Fe 3d states are localized in Cs, because of the large lattice constant of Cs host.

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 the 1Fe/5Pd ML structure, of which the stacking unit is the face-centered-cubic unit cell of Pd. We show for Pd sites only the 4d DOS. The exchange splitting of the Fe 3d band is still large at ~ 3 eV, and the spin magnetic moment of Fe ion is $\mu_S = 3.12\mu_B$ in Pd. Both values are similar in size to those of Fe in Cs. However, the orbital magnetic moment of the Fe ion is negligible,

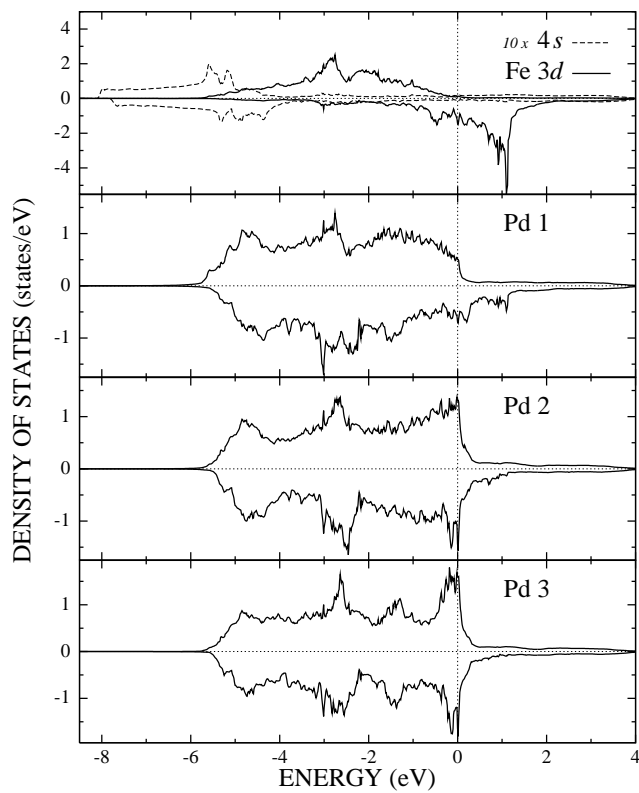


FIG. 2. The LSDA DOS of the 1Fe/5Pd ML structure. The 4d DOS is shown for Pd. The hybridization of Fe 3d bands with Pd 4d is large, and so the orbital magnetic moment of Fe is negligible. The spin magnetic moment of the first NN Pd is non-negligible, $0.30\mu_B$.

$\mu_L = 0.09\mu_B$ in Pd. The 3d orbitals of Fe are greatly deformed by the hybridization with Pd, and so Fe loses most of its ionic nature. 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 [13]. The 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 8 times larger than the bcc unit cell of Cs. The supercell has one Fe atom at the center and 15 Cs atoms at the right sites. Considering that the Fe-Fe interaction becomes negligible over $2a = 12.10 \text{ \AA}$, 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 and 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

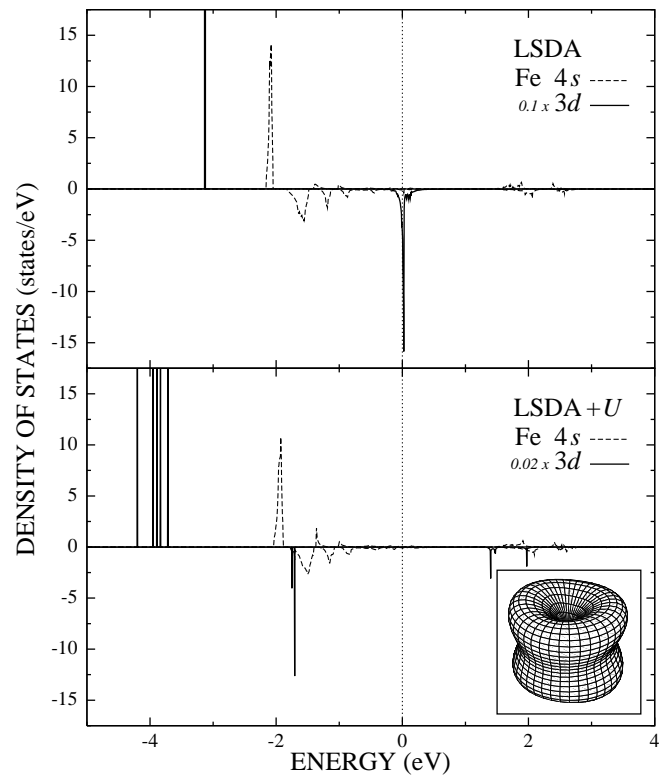


FIG. 3. The LSDA (upper panel) and the LSDA + U (lower panel) DOS's of Fe in the supercell structure. The magnitudes of the spin-up bands of Fe 3d are arbitrary. All the Fe bands, both of Fe 4s and 3d, are localized. In the LSDA, one notices a small energy dispersion of the spin-down bands of Fe 3d near E_F due to the hybridization with Cs 6s bands. In the LSDA + U , Fe 3d levels are split by the Coulomb correlation and the spin-orbit interactions. Angular distribution of the occupied spin-down states of Fe 3d (inset) indicates that Fe 3d states are well localized.

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 also become localized in the supercell.

We summarize the calculated magnetic moments in Table I. Because of charge transfer from Cs sites, the 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. Hence the electron configuration of the Fe ion is close to $3d^7$ in the LSDA + U calculation. While the transferred charge reduces the spin magnetic moment of the Fe ion, the reduced spin magnetic moment is compensated by the enhanced orbital magnetic moment. The obtained $3d^7$ configuration for Fe impurity in Cs is in agreement with existing calculations for Fe impurities in alkali metal hosts [14,15], but differs from the experiment of the $3d^6$ configuration by the time differential perturbed γ -ray distribution method [4]. The analysis of the experiment, however, depends on the model parameters, and

TABLE I. The calculated magnetic moments (μ_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	Cs
LSDA	3.29	μ_S	3.59	-0.29
LSDA + SO	4.62	μ_S	3.54	-0.51
		μ_L	1.60	-0.01
LSDA + U	6.43	μ_S	3.14	0.42
		μ_L	2.90	-0.04

so the interpretation is rather ambiguous. Therefore, to determine the correct valence state of the Fe ion, more direct methods such as the x-ray absorption spectra or the Mössbauer effect are desirable. Further, experimental tools which measure separately spin and orbital moments, such as the magnetic circular dichroism and the resonant x-ray magnetic scattering method, are demanded.

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 ~ -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 the Fe ion itself rather than from the induced spin polarization of neighboring Cs atoms. In this sense, $3d$ electrons of Fe in Cs should be treated as $4f$ electrons in rare-earth ions. The small discrepancy from the experiment ($\sim 7\mu_B$) is thought to arise from improper use of $g_J = 2$ in the analysis of the experiment [1], which counts only the spin contribution.

It is noteworthy in the experiment [1] that neither the moment change between Fe ions on the surface and in the bulk nor the Fe coverage effects 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, which yields enhanced magnetic moments. For Fe impurities in Cs films, Fe ions are already fully localized in the bulk, and thus no further localization of Fe electrons will occur on the surface. The negligible Fe coverage effects can be understood consid-

ering the short interaction range ($2a = 12.10 \text{ \AA}$) 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.

Finally, some remarks are made on Co impurities in Cs. For Co impurities in the supercell structure of Cs, we have obtained the total magnetic moment of $M = 5.81\mu_B$ in the LSDA + U . The magnetic moment of Co ion ($\mu_S = 2.08, \mu_L = 2.94$) is consistent with the $3d^8$ electronic configuration. The contribution from Cs atoms to the total magnetic moment is slightly enhanced to $\sim 13\%$, which arises from the increased hybridization between Co $3d$ and Cs $6s$. A too large observed magnetic moment $\sim 8\mu_B$ for Co impurities [1] is again attributed to the improper use of spin only g_J .

In conclusion, Fe impurities in Cs films have different behavior from those in Pd films in that the giant magnetic moments of Fe impurities in Cs originate mainly from the localized Fe ions but not from the induced spin polarization of 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. Both the Coulomb correlation and the spin-orbit interaction at the Fe site should be properly considered to get consistent results with experimental data.

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