Electronic structure of s, p - and $3d$ -element impurities in ferromagnetic Fe

J. H. Park and B. I. Min

Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

(Received; May 1, 1998 Accepted; August 26, 1998)

Using the self-consistent tight-binding-linear-muffin-tin-orbital (TB-LMTO) recursion method, we have investigated the rearrangement of electronic structures with the addition of both s, p -element (Al , Si , and P) and $3d$ -element impurities in bcc ferromagnetic Fe. We have obtained local density of states (LDOS), charge transfers, and magnetic moments. In the case of s, p -element impurities, we have found that the s -level LDOS at the impurity site has a dip in the vicinity of the bare d -level of the host, which is related to the Fano anti-resonance. We have also found that the simple dilution model for the impurity works well for Al , Si , and P impurity in Fe. As for transition metal (TM) impurities, we have found that early TM impurities ($Ti - Cr$) favor antiferromagnetic arrangements with respect to the host Fe spins, while late TM impurities ($Mn - Ni$) favor ferromagnetic arrangements.

Key words: s, p -element impurity, $3d$ -element impurity, bcc Fe, electronic structure, magnetic moment

1. Introduction

For long times, Fe-based systems have attracted much attention due to their desirable features such as a large saturated magnetic moment and the Invar character [1–3]. Since Friedel's study on transport properties of alloys based on the virtual-bound-state model, the problem of impurities in metals has been studied for more than 40 years. The introduction of impurities changes the electronic structure of the host by perturbing the electronic charge distribution as well as the positions of the neighboring host atoms.

In this study, we have investigate the rearrangement of the electronic and magnetic structures in the ferromagnetic Fe with the addition of impurity atoms. We have considered both non-transition metal s, p elements (Al , Si , and P) and $3d$ transition metal (TM) element impurities. We have examined the mechanism of changes in the electronic structure and the saturated magnetic moments of host Fe atoms with adding impurities.

To explore the above problem, one needs an accurate and reliable method which can describe electronic structure of systems without translation symmetry. The supercell method is often used by restoring the periodicity, but it requires much CPU time due to its large unit cell. One of the reliable and accurate first principles technique for describing disordered systems is the tight-binding linear-muffin-tin orbital (TB-LMTO) recursion method [1,4,5]. In this paper, we have employed the TB-LMTO-recursion (TB-LMTO-R) method to determine electronic

structures of both non-TM and TM element impurities in bcc Fe.

The procedure of the present calculation is essentially the same as shown in previous paper [7], which makes use of the formalism developed by Andersen and coworkers. The impurity atom is placed at the center of a 9216-atom bcc cluster. The cluster is constructed so that 26 levels of recursion coefficients can be calculated exactly when we include up to third-nearest-neighbor interactions. To simplify the calculation, it is assumed that positions of host Fe atoms are not relaxed.

2. s, p -Element Impurities

For s, p -element impurities, calculations were carried out for impurities of Al , Si , and P in bcc Fe. Figure 1 shows the LDOS at the impurity and its neighboring Fe sites. With increasing the valence electrons at the impurity atom (as varying from Al to P), the split-off local level below the band bottom moves down in energy, while the split-off local level for Al impurity is not distinguishable because of smearing with host states. One can notice dips in s -projected LDOS at the impurity atom near -4.1eV and -2.3eV for the spin-up and the spin-down band, respectively. This dip corresponds to the $s(Al) - d(Fe)$ Fano antiresonance, where the bond order changes sign [7,8]. It means that the character of the wave function changes from a bonding state to an antibonding state at this energy. This antiresonance features are well appeared for the case of weak $s-d$ coupling. The $s-d$ coupling in the present case is about 40% of $s-s$ coupling. Another interesting feature in Fig. 1 is that no essential difference is found in the dip positions of the s -band LDOS's amongst Figs. 1(a)–1(c). The invariance of the dip position is due to a cancellation between the strength of the $s-d$ hopping and the orbital energy variance.

The LDOS of neighboring FeI site is not much perturbed from the original LDOS of bcc Fe, as shown in Fig. 1(d). Accordingly, the number of states at neighboring Fe sites is not changed much from that in bcc Fe. The another change of the FeI LDOS as compared to the LDOS of bcc Fe is the downward shift of the spin-down band, implying that the spin-down band gets more electrons from the impurity atoms than the spin-up band does (see Table I). By comparing the FeI LDOS with the bcc Fe LDOS, we note that the FeI LDOS is a bit wider and located lower in energy than the bcc Fe LDOS.

In Table I, we present magnetic moments of $3d$ and

FIG. 1. LDOS of s, p -element impurities(M) in bcc Fe. (a) $M=Al$; (b) $M=Si$; (c) $M=P$. Dotted, dashed, and solid lines are s , p , and total LDOS, respectively. (d) LDOS of neighboring FeI site(solid line) as compared with that of pure bcc Fe(dotted line). The Fermi level is at 0.0 eV.

$s + p$ electrons at different sites. We note that the magnetic moment of the nearest neighbor FeI site is reduced as compared to that of bcc Fe ($2.06 \mu_B$ in the present calculation), because of a charge transfer from the impurity site. We also note that magnetic moments of $3s + 3p$ electrons are polarized antiferromagnetically with respect to that of $3d$ electrons of host Fe. Magnetic moments of these $3s + 3p$ bands are induced by the hybridization with $3d$ orbitals. The moment reduction at FeI sites can be understood by noting that the Al atoms play a role as hopping sites for $3d$ electrons, that is, the existence of Al atom helps itinerancy of conduction electrons. This effect spreads the band width, and in turn suppresses the exchange-splitting. At the next nearest neighbor (NNN) $FeII$ sites, magnetic moments are enhanced as compared to that of bcc Fe in all the cases. By comparing the $FeII$ LDOS with the bcc Fe LDOS, we note that the $FeII$ LDOS has a narrower and much higher peak than the bcc Fe LDOS. Therefore, the hopping of electrons at $FeII$ sites becomes weaker than that at the bcc Fe site. This suggests that the strong hybridization between the

TABLE I. Local magnetic moments $m[\mu_B]$ at the impurity, nearest neighbor (NN), and next nearest neighbor (NNN) Fe sites.

Impurity elements	Al	Si	P
Impurity			
m_{3s+3p}	-0.125	-0.123	-0.112
NN Fe			
m_{3d}	1.971	1.932	1.882
m_{4s+4p}	-0.045	-0.042	-0.047
m_{total}	1.927	1.891	1.834
NNN Fe			
m_{3d}	2.247	2.222	2.151
m_{4s+4p}	-0.074	-0.044	-0.05
m_{total}	2.213	2.178	2.101

impurity and FeI sites may induce a weak interaction between FeI and $FeII$, and then lead to the magnetic moment enhancement at $FeII$ sites.

When we consider the average magnetic moments of neighboring Fe sites in the case of Al impurity, $2.05 \mu_B (= 1.927 \mu_B \times 8 + 2.213 \mu_B \times 6) / 14$, the average magnetic moment of Fe is changed by only 0.5% from that of bcc Fe ($2.06 \mu_B$), which is in good agreement with experiments [3]. Therefore, it is expected that the dilution model works well for Al , Si , and P impurity in bcc Fe, in view of comparatively small perturbation at $FeII$. Namely, impurity effects are localized within the impurity site, and so the simple dilution model is acceptable for Al , Si , and P .

3. 3d Transition Metal Element Impurities T

We have performed TB-LMTO-R electronic structure calculations for the 3d TM element impurities in the ferromagnetic bcc Fe. The notable difference of LDOS between 3d-element and s, p -element impurities is the appearance of the 3d-resonance of the impurity atom, which is overlapped with the 3d-band of Fe. The hopping between the 3d-band of the impurity and the 3d-band of Fe is so strong that LDOS of FeI sites is much perturbed from that of bcc Fe.

In Table II, we present results for the magnetic moments of impurity atoms. It is seen that magnetic moments of early TM impurities ($Ti - Cr$) are polarized antiferromagnetically with respect to that of host Fe, while magnetic moments of late TM impurities ($Co - Cu$) are polarized ferromagnetically.

The magnetic moment of Mn is polarized ferromagnetically in the present calculation, but the previous report [9] gives an antiferromagnetic polarization. It may be due to so high LDOS at E_F at the Mn impurity site, and so the numerical calculation is unstable to yield two different stable magnetic phases. The virtual levels (the, so called, 3d resonance bands) are characterized by high

TABLE II. Local magnetic moments $m[\mu_B]$ at the impurity and Fe site.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
m_{Imp}	-0.57	-1.00	-0.94	1.90	2.12	1.69	0.90	0.18
m_{Fe}	1.96	1.99	2.07	2.04	2.12	2.18	2.21	2.14

DOS in the energy spectrum. Thus, whenever Fermi electrons have access to the virtual levels, there occur profound effects on the electronic transport and related properties of the dilute alloys. The virtual levels are shifted down as filling up electrons in the d -level of the impurity atom. Thus, virtual levels of early TM impurities are above E_F , while those of late TM impurities are below E_F . The virtual level of the *Mn* impurity located at E_F . From this, one can expect a possible structural instability in the case of *Mn* impurity in *bcc* Fe.

LDOS for early TM impurities (*Ti* – *Cr*) shows that the position of the spin-up virtual level is lower than that of the spin-down virtual level. But the number of occupied spin-up electrons is less than that of occupied spin-down electrons, indicating that early TM impurities (*Ti* – *Cr*) prefer to polarize antiferromagnetically to the host Fe. This feature can be understood as follows. For early TM impurities, the hopping parameters for spin-down electrons are larger than those for spin-up electrons. Indeed, more occupancy in the spin-down band arises from the larger hopping parameters. That is, the spin-down band is broadened more than the spin-up band to have more tail part below E_F . For late TM impurities (*Co* – *Cu*), the $3d$ -levels for both spin directions are located below E_F , and there are more spin-up band states within the impurity WS sphere than the spin-down band states. The impurity atom has a different nuclear charge as well as a different atomic volume from the surrounding host atoms. These differences force a redistribution of electronic charge around the impurity site. The amount of charge transfer q ($q \equiv N_l - Z$) within the WS sphere of the impurity and neighboring Fe sites is given in Fig. 2. It shows the oscillating behavior as a function of the distance from the impurity site, which is reminiscent of the Friedel Oscillation. The difference in the local charge at each impurity site can be partly understood based on the difference of the electro-negativity between the impurity and the host atoms. For late TM impurities (*Co* – *Cu*), the impurities gain charges, mainly spin-down electrons, from neighboring Fe sites. Therefore, neighboring Fe sites for the case of late TM impurities have enhanced magnetic moments, in contrast to the case of early TM impurities as shown in Table II. There is an exception for the *Mn* impurity. As mentioned above, High DOS at E_F for the *Mn* impurity may yield a structural instability.

Acknowledgments— This work was supported by the MST fund, and in part by the POSTECH-BSRI program (BSRI-97-2438). Helpful discussion with Y.V. Skrypnik

FIG. 2. Local charge redistribution for $3d$ TM impurities in *bcc* Fe. The x-axis represents the distance from the impurity site in unit of the nearest neighbor distance.

is greatly appreciated.

References

- [1] H. J. Nowak, O. K. Andersen, T. Fujiwara, and O. Jepsen, *Phys. Rev.* **B44**, 3577 (1991).
- [2] T. Fujiwara, *J. Phys. F; Met. Phys.* **12**, 661 (1982).
- [3] A. T. Aldred, *J. Phys. C: Solid State Phys.* **1**, 1103 (1968).
- [4] O. K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53**, 2571 (1984).
- [5] O. K. Andersen, O. Jepsen, and D. Glotzel, in *Highlights of Condensed-Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi, North-Holland, New-York, (1985).
- [6] V. Heine, R. Haydock, and M. Kelly, in *Solid State Physics Vol.35*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic press, New York, 1980).
- [7] J. H. Park, Y. V. Skrypnik, and B. I. Min, submitted.
- [8] K. Terakura, *J. Phys.* **F7**, 1773 (1977).
- [9] O. Yu. Kontsevoi and V. A. Gubanov, *Phys. Rev.* **B51**, 15125 (1995).