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The effect of Si on the local magnetic moment and hyperfine interaction of BCC-Fe

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Abstract. The electronic structure and local magnetic properties of disordered Fe-rich Fe–Si alloys were calculated using the first-principles self-consistent cluster method. The calculated local magnetic moment, isomer shift and hyperfine field are compared with the existing experimental results. The Fe 3d magnetic moment was found to decrease with the number of Si atoms appearing in the first and second neighbouring shells. The isomer shift increases and the hyperfine field decreases in magnitude with an increasing number of Si atoms in the cluster.

1. Introduction

The substitution of the Fe atom by Si or Al in metallic BCC-Fe is considered to be the best known example of simple dilution behaviour. This means that introducing Si atoms into the iron matrix does not disturb the original magnetic structure [1]. This statement is based on the observation that the magnetization of Fe–Si decreases linearly with the gradient of $d\mu/dx = -2.2\mu_B$ for small concentrations of the substituted atom.

Such a picture seems, however, to be oversimplified, as it has already been shown [1] that the decrease in the average hyperfine field is remarkably slower than the magnetic moment of the Fe–Si alloy, which can be taken as an indication that substitution of Fe by Si causes some additional changes in the spin density as seen by the Fe nucleus which would thus affect the magnetic moment at the Fe site. Early experiments [2] have shown that the magnetic moment of Fe in the Fe–Si alloy is influenced by the neighbouring Si atoms. It increases with increasing Si content below 8 at.% Si but decreases rapidly above this concentration. Similar behaviour was also found in the Fe–Al alloys [4].

Dubiel and Zinn [3] have studied in detail the influence of Si on the spin and charge density in BCC-Fe containing up to 13 at.% Si by means of Mössbauer spectra. They established the correlations between changes in the isomer shift (IS) and hyperfine (HF) field due to one or more Si atoms and found that the HF field was reduced, but that the IS was increased by the presence of neighbouring Si atoms.

The possibility of theoretically interpreting such local magnetic properties stimulates a microscopic description of the disordered Fe–Si alloy, by which it is hoped to answer the following questions. (i) Is the local magnetic moment at the Fe site influenced by the (next) neighbouring Si atoms and if so by what mechanism? (ii) Why

and how are the IS (charge density) and HF interactions (spin density) related to the (next) neighbouring Si atoms? We undertake an investigation of the electronic structure and magnetic properties at the Fe site by means of the SCF-LCAO-MO method, which has proved to be a very powerful technique for systems with reduced symmetry [5] that are intractable for conventional band structure calculations.

2. Theoretical approach

Clusters with 15 atoms, as depicted in figure 1, were considered to represent the undistorted BCC-Fe matrix. The cluster consists of eight nearest neighbours (NN) and six next nearest neighbours (NNN). The influence of the Si was studied by substituting two to eight NN Fe atoms and four NNN Fe atoms, which are used to represent disordered Fe-Si alloys with a small Si concentration. In all cases the cluster was embedded in the iron crystal. For convenience, we use the nomenclature $C(N, M)$ to represent the cluster with N NN Si atoms and M NNN Si atoms.

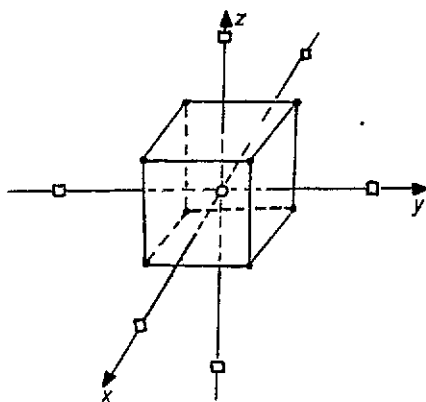


Figure 1. The geometry of Fe_{15} cluster for BCC-Fe: O, central site; ●, NN; ◇, NNN.

The electronic structure of the clusters were calculated with the first-principles discrete variational method (DVM) within the local density functional theory [7]. The same method has been employed in several other calculations on metal clusters [8, 9], and was previously described in detail in [10].

The spin-polarized one-electron equation

$$(h_{\sigma} - \epsilon_{j\sigma})\phi_{j\sigma}(\mathbf{r}) = 0 \quad (1)$$

are solved self-consistently, where wavefunctions $\phi_{j\sigma}(\mathbf{r})$ for different spins σ are allowed to have different spatial extensions. The one-electron Hamiltonian, in atomic units, is

$$h_{\sigma} = -\frac{1}{2} \nabla^2 + V_{\text{Coul}}(\rho_{\sigma}) + V_{\text{xc}}(\rho_{\sigma}). \quad (2)$$

The electronic density at point \mathbf{r} is a sum over the molecular spin-dependent orbitals $\phi_{j\sigma}$ with occupation $n_{j\sigma}$

$$\rho_{\sigma}(\mathbf{r}) = \sum_j n_{j\sigma} |\phi_{j\sigma}(\mathbf{r})|^2. \quad (3)$$

$V_{xc}(\rho_{\sigma})$ was chosen to be of the spin-polarized von Barth-Hedin form [11].

In the DVM the molecular orbitals are expanded on the basis of numerical atomic orbitals (LCAO). Spherical potential wells around the atoms are employed to obtain more contracted valence orbitals and these include the 3s, 3p, 3d, 4s, 4p orbitals for the central Fe, 3d, 4s, 4p for other Fe atoms and 3s, 3p for the Si. Other low-lying orbitals are kept frozen in. The secular equation $(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0$ are solved self-consistently using matrix elements determined by numerical integrations on a three-dimensional grid. In the usual DVM, a random integration method (diophantine) [10] is employed; however, in the case of HF interactions, the calculations require much greater caution in the numerical procedures, especially at the core region of the probe atom, where accurate matrix elements for the rapidly varying functions are difficult to achieve. Thus a special integration scheme in spherical volumes about a particular atom was developed [5]. In the present work, we are primarily interested in the HF fields of the central Fe atom and have replaced the diophantine points in the core region by a dense regular (angular \times radial Gaussian quadrature) mesh.

In the self-consistent-charge (SCC) approximation, the actual electronic density is replaced by a model density $\rho_{\sigma}^{\text{SCC}}(\mathbf{r})$, which is a superposition of radial densities R_{nl}^{ν} , centred on the cluster atoms via a diagonal-weighted Mulliken population f_{nl}^{ν}

$$\rho_{\sigma}^{\text{SCC}}(\mathbf{r}) = \sum_{nl} \sum_{\nu} f_{nl}^{\nu} |R_{nl}(\mathbf{r}_{\nu})|^2. \quad (4)$$

Finally, an embedding scheme [10] is employed to simulate the effect of the rest of the microcrystal on the cluster. It consists basically of placing numerical atomic potentials at about 300 of the nearest sites surrounding the cluster.

The IS of an absorber A relative to a source S in a Mössbauer nuclear-gamma-resonance measurement is given by (see for example [12])

$$\text{IS} = \alpha \{ \rho_A(0) - \rho_S(0) \} \quad (5)$$

where α is called the IS calibration constant. For ^{57}Fe , the reported values of α vary from -0.11 to $-0.51 a_0^3 \text{ mm s}^{-1}$, where a_0 is the Bohr radius. We took $\alpha = -0.25 a_0^3 \text{ mm s}^{-1}$ which is close to recent estimates [13]. We have neglected 1s and 2s contributions since the computed difference in $\rho(0)$ for these orbitals in different environments is negligible [5].

The HF magnetic field as seen by the probe nucleus is given by [14]

$$H_c = \frac{2}{3} \pi g \mu_B \frac{\langle S \rangle}{P} \{ \rho_{\uparrow}(0) - \rho_{\downarrow}(0) \} = B \Delta \rho(0) \text{ (kG)} \quad (6)$$

where S is the total spin of ion with P unpaired electrons, g is the electronic g factor, μ_B is the Bohr magneton. $\rho_{\uparrow}(0) - \rho_{\downarrow}(0)$ is the spin density at the nucleus which was calculated respectively for spin-up and spin-down, B is a constant and equal to $524.2 \text{ kG}(e/a_0^3)^{-1}$.

3. Results and discussions

3.1. Charge and spin distribution

Since the central atom in a cluster has all its NNs and NNNs present, it should represent the corresponding properties of the bulk solid better than an atom in the outer coordination shells would. This has been confirmed by many calculations on metallic clusters [8, 9] and is in accordance with intuition.

We have used several distinct clusters to study the local magnetic moment at the Fe site and its changes as Si atoms are substituted for the Fe atoms at the NN and NNN shells. To preserve some symmetry, we replace two Fe atoms with two Si at any one time. In table 1, we present the 3d and 4s + 4p magnetic moment at different sites, which were calculated by taking the difference of the spin-up and spin-down Mulliken populations [15].

Table 1. Local magnetic moment of different site in cluster. $C(N, M)$ indicate cluster with N and M Si atoms at NN and NNN shells.

Cluster symmetry	C(0,0) O _h	C(2,0) D _{3d}	C(4,0) T _d	C(6,0) D _{3d}	C(8,0) O _h	C(0,4) D _{4h}
Central Fe						
$\mu_{3d}(\mu_B)$	3.20	2.81	2.48	1.92	-0.49	3.05
μ_{4s+4p}	-0.39	0.03	0.27	0.33	-0.31	0.09
Total	2.81	2.84	2.75	2.25	-0.80	3.14
d charge	6.66	6.66	6.67	6.60	6.71	6.67
NN Fe						
μ_{3d}	3.67	3.62	3.62	3.55		3.36
μ_{4s+4p}	0.27	0.10	0.37	0.57		0.08
Total	3.94	3.72	3.97	4.12		3.44
d charge	6.22	6.22	6.23	6.29		6.19
NNN Fe						
μ_{3d}	3.79	3.72	3.61	3.51	3.46	
μ_{4s+4p}	0.46	0.52	0.63	0.46	0.67	
Total	4.25	4.24	4.24	3.97	4.13	
d charge	6.15	6.15	6.20	6.21	6.23	
Si						
μ_{3s+3p}		-0.33	-0.30	-0.40	-0.25	-0.06

We find that, for the pure iron cluster $C(0,0)$, the total magnetic moment at the central site, $2.81\mu_B$, is significantly larger than the experimental value $2.2\mu_B$. As noted earlier for other magnetic materials, [8, 9] this is a finite cluster effect. Since truncation of the cluster does not allow sufficient delocalization of the wavefunction in the solid to take place on the cluster surface, the moments tend to be more atomic-like. The fact that the magnetic moment increases outwardly from the centre to the NNN site (see table 1) is also another surface effect, although we used an embedding scheme to make the surface atoms (NNN atom in our calculation) experience a potential similar to the real crystal potential. However, the central Fe is the most bulk-like atom and as we take more atom shells into account the cluster size effect can be reduced. Many

calculations have indicated that, for most physical properties, the 3-4 atomic shell cluster is an appropriate choice [5, 6, 17].

We note that the 3d moment of the central site decreases with the number of Si substitutions in the NN shell, and it becomes negative when all the NN Fe have been substituted in the C(8,0) cluster. This may not be possible for Fe-rich Fe-Si alloys with eight Si atoms as first neighbours, but as a theoretical model and a natural extension of studies, it is very interesting. Kouvel [4] has found that the Fe site moment collapsed when there were eight NN Al atoms, and Dubiel *et al* [3] have pointed out that the influence of the Si atoms on the charge and spin density is more significant than that of the Al atom. Thus our calculation results are reasonable and in agreement with experiment. It can be seen that the total magnetic moment of the central Fe atom does not decrease as rapidly as the 3d moment; instead, it increases a little in the C(2,0) cluster. This trend is well consistent with experiment [2].

On observing the 4s + 4p moment, the itinerant moment, we note that it is negative in the pure Fe cluster C(0,0) and becomes positive in the C(2,0), C(4,0), C(6,0) and C(0,4) clusters. The magnetic moment of these valence bands are induced by hybridization of the orbitals of the valence and 3d bands. These have been found to be negative experimentally [16] in BCC-Fe and are sensitive to the environment. Since the s and p electrons interact antiferromagnetically with the neighbouring d electrons, as pointed out by Anderson and Clogsten [16], the s-d and p-d interactions thus lead to a negative (4s + 4p) moment. With the appearance of the Si atoms in the first and second shells and because the Si atoms have a negative moment (see table 1), the (4s + 4p) moment starts to change from negative for the pure Fe cluster C(0,0) to positive for the C(2,0) cluster and to increase steadily as *N* increases. However the situation in the C(8,0) cluster is a different case, where the 3d magnetic moment of the central Fe atom also changes the direction and thus the (4s + 4p) moment is negative.

When the Si atom is located in the NNN shell, in C(0,4), we note that its effect on the moment of the central atom is much less than that of the C(4,0) cluster, thus the d magnetic moment is quite localized.

In all cases of the C(*N*,0) cluster, we find a small negative moment for the Si atoms, which is primarily induced by hybridization of the Si 3p and Fe 3d orbitals, as we will discuss later. In order to calculate the magnetic moment of the Si atom in the cluster accurately, we studied the SiFe₁₄ cluster, where the central Fe was replaced by Si. The results are listed in table 2. For comparison, we also give the values of cluster C(0,0). It should be noted that the Si atom in the matrix of the BCC-Fe has a negative moment about $-0.73\mu_B$, which is larger in magnitude than the NN shell Si which is about $-0.33\mu_B$ due to much significant hybridization.

Table 2. Magnetic moment of the Fe₁₅ and SiFe₁₄ clusters.

Cluster	Central μ_d/μ_{3d+3p}	NN μ_d	NNN μ_d
Fe ₁₅	3.20	3.67	3.79
SiFe ₁₄	-0.73	3.65	3.77

To find the reasons for the reduction in the 3d moment, we note that the d charge on the central site is almost constant from one cluster to another, which indicates that

the charge transfer between the Si and Fe is not responsible for the reduction in the d moment. In our opinion, it is due to electron transfer from spin-up to spin-down. A qualitative picture of this is given in the following section.

3.2. Density of states

The energy spectrum of the valence eigenfunctions is best displayed as a density of states (DOS). The contribution of state nl of atom v to the DOS is represented by

$$D_{nl}^v(E) = \sum_p f_{nl,p}^v \frac{\sigma/\pi}{(E - \epsilon_p)^2 + \sigma^2} \quad (7)$$

where $f_{nl,p}^v$ is the Mulliken population contribution to the p th molecular orbital. The Lorentzian width parameter σ was chosen to be 0.1 eV. The total DOS in the DVM-MO method consists of contributions from all the atoms in the cluster and is not as accurate and instructive as the partial DOS of the central atom. Thus we have only depicted the 3d DOS of the central atom in figure 2.

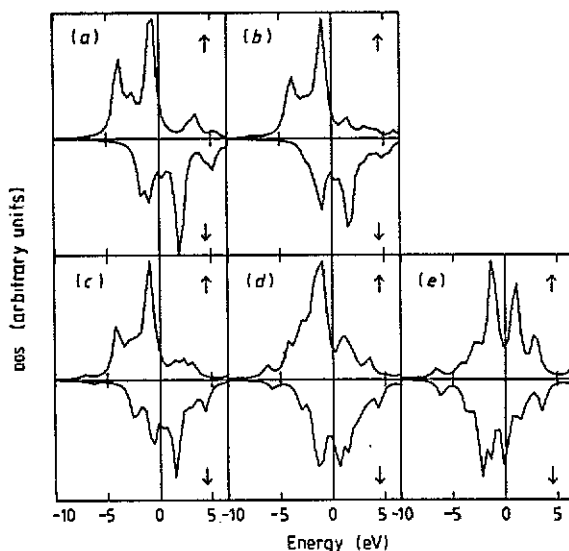


Figure 2. 3d DOS of central Fe in (a) C(0,0), (b) C(2,0), (c) C(4,0), (d) C(6,0) and (e) C(8,0) clusters.

The 3d DOS of C(2,0) and C(4,0) clusters with two and four Si atoms in the NN shell do not differ noticeably from the C(0,0) cluster, but the situation in C(6,0) and C(8,0) is quite different, as two main peaks of majority spin tend to become one sharper peak. The minority band suffers similar changes due to the substitution of the Si atoms in the Fe matrix but the major peak is broadened and moves to a lower energy. The energy split between the main (majority and minority) 3d peaks decreases with respect to a decrease in the magnetic moment. The hybrid states of Si 3p and Fe 3d appear in figures 2(d) and (e) at about -4 eV for the majority band and -3 eV for the minority band.

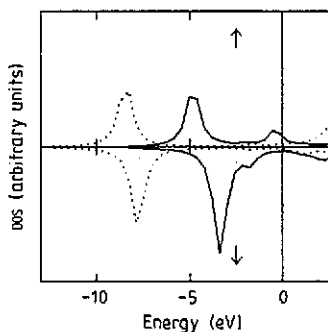


Figure 3. Si 3s and 3p DOS for SiFe_{14} cluster: full line, 3p; dotted, 4p.

The 3s and 3p partial DOS of the SiFe_{14} cluster are presented in figure 3. The 3s band is lower at about -8 eV and impossibly overlaps with the Fe 3d band. However, the Si 3p band at about -3 to -4 eV may hybridize greatly with the 3d band.

From these discussions, we can provide a qualitative description of the reduction in the Fe 3d magnetic moment when there are Si atoms in the neighbouring shells. The majority are formed from the bonding and antibonding interactions of the Si 3p and Fe 3d electrons. There are two sets of p-d hybrids belonging to majority and minority spin. Since the majority band is almost fully occupied (see figure 2(a)), the p-d hybrids corresponding to majority spin cannot accommodate all the electrons in the bonding states and some of these have to occupy an antibonding state. If these antibonding states are above the Fermi energy, the majority electrons occupying these states would fall to lower states in the minority band. This transfer would set up a mechanism for converting majority spins into minority spins resulting in a reduction in the magnetic moment while maintaining the total d charge.

Another factor involved in the reduction of the magnetic moment at the Fe site can also be obtained by observing the DOS. From figure 2(a) and other calculations [18], we find that the width of the minority 3d band is wider than the majority 3d band, and the Si 3p minority band is higher than the majority 3p band, see figure 3. This means that the interactions of the d_{\downarrow} electrons and p_{\downarrow} electrons are stronger than those of d_{\uparrow} and p_{\uparrow} . Hence the d_{\downarrow} band potential was lowered by the p-d interactions compared with the d_{\uparrow} band and thus the majority spins flow to the minority band, reducing the moment at the Fe site.

3.3. Isomer shift and HF field

The IS is a measure of depletion or accumulation of electronic charge at the probe nucleus. We have calculated the IS relative to pure iron according to equation (5) for $C(N, M)$ clusters and the results are listed in table 3.

It is noted that the IS is a small positive value indicating there are small charge transfers in the Fe-Si disordered alloy in accordance with the Mulliken analysis discussed earlier. The IS is proportional to the numbers of Si atoms in the NN shell, which means the charge density at the Fe nuclei is reduced by the Si atoms. Dubiel *et al* [3] have found that the IS relative to BCC-Fe caused by one Si atom is about 0.05 mm s^{-1} when the Si atom is located in the NN shell and is about 0.001 mm s^{-1} when the Si is in the NNN shell. We calculated the IS/Si atom and listed the results in the fourth entry in table 3, which is in good agreement with experiment. Our calculation

confirmed the reduction in the charge density at the Fe nucleus due to introducing the Si atom in the BCC-Fe which is clearly shown in the spin density in table 3. This is consistent with the difference in the electronegativity of Fe (1.82) and Si (1.90). However, the small electronegativity difference may only account for the calculated IS because the s-electron transfer according to the Mulliken population is only about 0.05. It is noted that the IS is dependent on the Mulliken population n_{j_s} and $|\phi_{j_s}(r)|^2$ (see equation (3)), hence the symmetry of the cluster may have a considerable effect on the s-wavefunction and IS. We have studied a C(4,0) cluster of C_{4v} symmetry, the IS of this cluster was found to be 0.381 mm s^{-1} , which is 0.07 mm s^{-1} larger than the T_d symmetry C(4,0) cluster. Therefore the IS is sensitive to the local environment.

Table 3. IS of Fe-Si clusters. N is the number of Si atoms in the cluster. $\rho(0)$ is $3s +$ valence charge density at the central Fe atom. $\alpha = -0.25 a_0^3 \text{ mm s}^{-1}$ was used to calculate the IS.

Cluster	C(0,0)	C(2,0)	C(4,0)	C(6,0)	C(8,0)	C(0,4)
$\rho(0)(a_0^{-3})$	146.888	146.245	145.645	145.222	144.856	146.612
IS (mm s^{-1})	0	0.165	0.311	0.416	0.508	0.044
IS/ N		0.083	0.078	0.068	0.070	0.01

The magnetic HF field H_{hf} of Fe is often regarded as a measure of the magnetic moment on the Fe site. Conveniently, it can be decomposed into two contributions for the transition metal [14]: (1) a large negative contribution due to the exchange polarization of the core electron by the d moment, referred to as the Fermi contact field; and (2) the contribution from the valence electrons.

We have calculated the HF field for six distinct local configurations representing the disordered Fe-Si alloys using equation (6). The valence contribution can be obtained directly from our self-consistent molecular orbital calculation and includes all occupied wavefunctions belonging to the totally symmetric representation of the cluster point group. But the core electron contribution requires greater caution because the HF interaction involves a delicate balance between the two big numbers for spin-up and spin-down density in the core region, and in the present cluster calculations, there is not enough variational freedom and numerical precision to obtain the core spin density. We used the atomic configuration obtained by Mulliken analysis to perform atomic self-consistent calculations in the X_α approximation. However, this approach has been employed for many cases [17, 6].

The calculated H_{hf} of pure BCC-Fe is 435 kG, which is significantly larger than the experimental value 339 kG. We would point out that, apart from the cluster size effect, both the atomic X_α treatment of the Fermi contact field and the relativistic effect can strongly affect the H_{hf} value.

Dubiel *et al* [3] have found that the HF field reduction due to one Si atom in the NN shell is $-27.0 \pm 0.8 \text{ kG}$, and is $-11.2 \pm 1.9 \text{ kG}$ due to one Si atom in the NNN shell of BCC-Fe. These values were found to be independent of the concentration of Si, indicating the localized character of the spin density which is dominantly determined by two neighbouring atomic shells. We also calculated this difference in the six different cluster using

$$\Delta H_{\text{hf}} = H_{\text{hf}}(\text{alloy}) - H_{\text{hf}}(\text{iron}) \quad (8)$$

Table 4. Hyperfine field of Fe-Si clusters. N is the number of Si atoms in the cluster. $\rho^{\uparrow}(0)(\rho^{\downarrow}(0))$ is $3s +$ valence spin-up (down) density at the Fe nucleus. H_c is the HF field of core electrons and $H_{hf} = H_c +$ contributions of valence electrons. μ_{Fe} and μ_d refer to the total and 3d moment of central Fe in the cluster. $B = 524.2$ kG $(e/a_0^3)^{-1}$ was used to calculate H_{hf} .

Cluster	C(0,0)	C(2,0)	C(4,0)	C(6,0)	C(8,0)	C(0,4)
μ_{Fe}	2.81	2.84	2.75	2.25	-0.80	3.14
μ_{3d}	3.20	2.81	2.48	1.92	-0.49	3.05
$\rho^{\uparrow}(0)(a_0^{-3})$	73.567	73.193	72.867	72.612	72.286	73.389
$\rho^{\downarrow}(0)$	73.321	73.052	72.778	72.610	72.587	73.223
$\Delta\rho_c(0)$	-0.767	-0.687	-0.543	-0.446	0.084	-0.753
$\Delta\rho_v(0)$	-0.064	-0.054	-0.002	-0.075	-0.290	-0.050
H_c (kG)	-420	-360	-285	-234	44	-395
H_{hf}	-435	-388	-286	-273	-196	-421
$\Delta H_{hf}/N$	—	23.5	37.3	27.0	30.0	-3.5

and listed the results in table 4. We found that, on average, one Si atom in the NN shell may reduced the H_{hf} by about 28 kG, which is in very good agreement with experiment. It seems that the effects previously mentioned which can affect the calculation of H_{hf} (iron) and H_{hf} (alloy) are partially cancelled when we calculate ΔH_{hf} . This may be responsible for the observed good agreement between our results and experiment. Our results for the C(0,4) cluster where the Si atom is in the NNN shell is not so good as C(N ,0) clusters because the atoms in the NNN shell are surface atoms in the cluster which are strongly affected by the embedding atoms. A larger cluster is desirable for calculating the effect of the NNN shell atoms.

It is worth pointing out that the H_{hf} decreases in magnitude with the number of Si atoms in the NN shell but the magnetic moment of the central Fe does not show this trend. This can be attributed to the ($4s + 4p$) moment which is negative in pure iron and becomes positive when there are Si atoms in the cluster. However the Fermi contact HF field H_c changes linearly with μ_d , shown clearly in figure 4. Therefore, the 3d magnetic moment is primarily related to the localized core spin density.

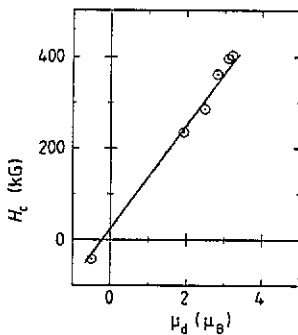


Figure 4. Correlation of the Fermi contact HF field and the 3d magnetic moment at the central Fe site.

4. Conclusion

We have calculated the electronic structure, local magnetic moment, IS and HF interactions of the Fe-Si disordered alloys by the self-consistent spin-polarized embedding molecular cluster method, and compared them with the existing experiment. Our results indicate the following conclusions

(1) The local moment of Fe is greatly influenced by the first shell Si atoms, and its value becomes negative when there are eight NN Si atoms. But the effect is considerably less when the Si atom is located in the second shell. The changes in the d moment is ascribed to the p-d overlaps in the Fe-Si alloy.

(2) The Fermi energy moves to the major peak of the 3d minority partial DOS, while exchange splitting is reduced by introducing the Si atom into the BCC-Fe.

(3) The calculated IS is positive indicating little charge transfer from the Fe to the neighbouring Si atoms, which is in good agreement with experiment. The local environment was found to have a considerable effect on the IS.

(4) The HF field is found to be negative and to decrease in magnitude with an increasing number of Si atoms in the neighbouring shells, which is consistent with experiment, indicating the spin-down density is reduced relative to the spin-up density. The H_{hf} is not proportional to the total magnetic moment of Fe but the contact field H_c is linearly related to the 3d moment.

When treating the disordered or impurity magnetic properties of transition metals, where the local order may be the dominant factor rather than the long-range periodicity, because these properties are chiefly determined by the quasilocalized d electrons, representation of the system by a small embedded cluster is not only computationally attractive but also physically reasonable. The cluster size may somewhat affect the absolute values of the calculated properties but the relative trend can be obtained quite accurately as shown in our studies, which is usually more important in the physical properties. Moreover, evidence [8] has been accumulated to show that as the cluster size increases the cluster model tends to the same limit as the band structure method.

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