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Analysis on the isomer shifts of β -FeSi₂ by molecular orbital calculations

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Abstract. The isomer shifts of undoped and transition-metal-doped compounds such as Co, Ni and Mn-doped β -FeSi₂ are discussed on the basis of molecular orbital calculation. From the LCAO SCF cluster calculation, the electron charge densities calculated $\rho(0)$ at iron nuclei of Fe I and Fe II sites are found to be consistent with isomer shifts as experimentally determined. On the basis of the Mulliken population analysis, it is disclosed that the 3d screening effect also plays an important role in determining the isomer shifts of both Fe sites in β -FeSi₂. Concerning Co-doped specimen, increases in the isomer shifts of both Fe sites with increasing Co concentration is observed; this experimental result can be interpreted as the lattice expansion due to the Co dopant, considering that the calculated $\rho(0)$ of both Fe sites is reduced on lattice expansion. However, the calculated isomer shift of the Fe I site results in a value larger than the experimental value; this implies that lattice expansion is anisotropic rather isotropic. Increases in the isomer shifts of both Fe sites in Ni or Mn-doped β -FeSi₂ are also observed, which is also interpreted as due to lattice expansion.

1. Introduction

Iron disilicide (β -FeSi₂) is an intermetallic compound showing semiconducting properties. β -FeSi₂ is an intrinsic semiconductor; Al- or Mn-doped β -FeSi₂ shows p-type semiconducting properties [1–4] whereas Co-doped β -FeSi₂ shows n-type semiconducting properties [1–3]. Since a p–n junction is easily formed in β -FeSi₂ and furthermore β -FeSi₂ is very stable to oxidation or heat, thermoelectric devices composed of β -FeSi₂ seem to have a great potential [5].

From a structural investigation [6], β -FeSi₂ is found to belong to the *Cmca* space group (orthorhombic system) and to be a very complex crystalline structure containing 48 atoms per unit cell (16 iron atoms and 32 silicon atoms). Concerning the atomic configuration of iron atoms, there exists two iron sites (namely Fe I and Fe II sites) with different atomic configurations [6]; the iron atom in each site is surrounded by eight silicon atoms with slightly different Fe–Si distances.

The Mössbauer spectrum of β -FeSi₂ was investigated by Wandji *et al* [7] and the isomer shifts for both Fe sites were determined from the calculation of the field gradient on the basis of the point charge approximation. The isomer shifts for the Fe I and Fe II sites are reported to be +0.01 mm s⁻¹ and +0.13 mm s⁻¹, respectively.

Certainly the Mössbauer spectrum for β -FeSi₂ was investigated, but the Mössbauer effect of Co-doped β -FeSi₂, which is industrially important, has not been studied. Hence we have investigated the Mössbauer spectrum of Co-doped β -FeSi₂ with a Co concentration range 1–3 at.% [8]. From the analysis of the Mössbauer spectra, especially the analysis of

the intensities, it is found that Co atoms occupy Fe II sites preferentially and the number of Co atoms occupying Fe II sites tends to increase with increase in Co concentration. The isomer shifts of both Fe sites obtained from curve fitting are greater than those obtained in undoped β -FeSi₂, showing proportionality to the Co concentration. Although the isomer shifts of β -FeSi₂ including the Co-doped specimen have been obtained experimentally, the estimate based on first-principles calculations has not been discussed.

Accordingly, we performed LCAO SCF calculations on the basis of a cluster model so as to estimate the isomer shifts in β -FeSi₂ quantitatively. In this article, on the basis of the LCAO SCF calculations, we mainly discuss the difference in between the isomer shifts of the two sites (Fe I and Fe II sites) and the dependence of the isomer shifts upon Co concentration, and furthermore we discuss the isomer shifts of other transition-metal-doped β -FeSi₂ compounds, such as Ni- or Mn-doped β -FeSi₂.

2. Calculation method

The clusters used for calculation are illustrated in figure 1, where the Fe I site corresponds to the Fe^ISi₈ cluster, and the Fe II site to the Fe^{II}Si₈ cluster. Each cluster is composed of one iron atom located in the centre and eight silicon atoms with slightly different Fe-Si distances, thus showing low symmetry.

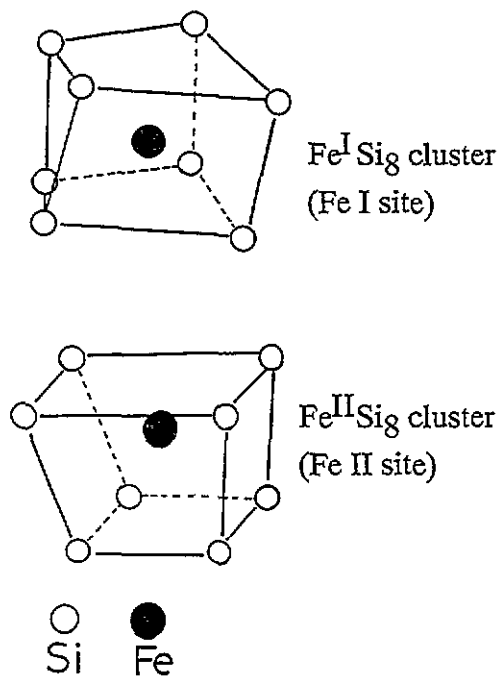


Figure 1. Fe^ISi₈ and Fe^{II}Si₈ clusters.

Ab-initio molecular orbital calculations were performed on both FeSi₈ clusters self-consistently using the program HONDO [9]. Since the magnetization of β -FeSi₂ is reported to be diamagnetic [10], we assume the spin quantum number S to be zero. It seems

very difficult to determine the appropriate number and equilibrium location of hydrogen termination because of the very complex crystalline structure; hence the silicon atoms have no hydrogen termination.

In the cluster calculation we use a total of 148 Gaussian functions contracted into 88 orbitals. The basis set for the iron atom is as follows: s state (1s to 4s), 15 Gaussians (four orbitals); p state (2p to 3p), eight Gaussians (six orbitals); d state (3d), five Gaussians (six orbitals). The basis set for the silicon atom is as follows: s state (1s to 3s), nine Gaussians; p states (2p to 3p), six Gaussians (six orbitals).

3. Computational results and discussion

3.1. Isomer shifts for the Fe^ISi₈ and Fe^{II}Si₈ clusters

Table 1 illustrates the calculated values of electron charge density $\rho(0)$ at the iron nuclei for the Fe^ISi₈ and Fe^{II}Si₈ clusters; the calculated $\rho(0)$ for Fe I and Fe II site are 10 849.393 au and 10 848.739 au, respectively. The dependence of the calculated $\rho(0)$ for both clusters upon the basis set is found to be very small; the dependence of the calculation results upon another basis set is considered to be negligible. The change in $\rho(0)$ by adding one more neighbour atom to the cluster is also found to be very small. The order of $\rho(0)$ seems somewhat smaller than the reported values ranging from about 11 600 to 11 900 au. This difference is supposed to be mainly due to the selection of the basis function of s orbitals composed of linearly combined Gaussian functions, especially the selection of the 1 s orbital.

Table 1. Calculated electron charge densities at iron nuclei $\rho(0)$, for Fe^ISi₈ and Fe^{II}Si₈ clusters.

	$\rho(0)$ (au)
Fe ^I Si ₈ cluster	10 849.393
Fe ^{II} Si ₈ cluster	10 848.739

As shown in table 1, $\rho^I(0) > \rho^{II}(0)$, where $\rho^I(0)$ and $\rho^{II}(0)$ are $\rho(0)$ for Fe^ISi₈ and Fe^{II}Si₈ clusters, respectively. The isomer shift S_{IS} is as follows:

$$S_{IS} = \frac{2\pi c}{3E_\gamma} Z e^2 \rho_{AS}(0) \Delta \langle r^2 \rangle \quad (1)$$

and

$$\rho_{AS}(0) = \rho_A(0) - \rho_S(0)$$

where E_γ is the γ -ray energy, Z is the nuclear charge, and $\rho_A(0)$ and $\rho_S(0)$ are the electron charge densities at the nuclei of the absorber and the source, respectively. $\Delta \langle r^2 \rangle$ is the difference between the mean square nuclear charge radius of the excited and ground states. Considering the experimental result of $S_{IS}^I < S_{IS}^{II}$, where S_{IS}^I and S_{IS}^{II} are the isomer shifts for Fe I and Fe II sites, respectively, we conclude that $\rho^I(0)$ should be greater than $\rho^{II}(0)$ by introducing $\Delta \langle r^2 \rangle < 0$ for ⁵⁷Fe nuclei into equation (1). Hence the above calculation result that $\rho^I(0) > \rho^{II}(0)$ is consistent with experiment, thus indicating that the isomer shift for each iron site determined by Wandji *et al* [7] is correct.

The isomer shift calibration constant α is defined as follows:

$$\alpha = \partial S_{IS} / \partial \rho_{AS}(0). \quad (2)$$

From our analysis of the Mössbauer spectrum for β -FeSi₂, the isomer shifts for Fe I and Fe II sites are +0.02 mm s⁻¹ and +0.14 mm s⁻¹, respectively [11], which are very close to the values reported by Wandji *et al* [7]. Accordingly, on the basis of equation (2), we obtain $\alpha = -0.18$ au mm s⁻¹, combining our above experimental results with the calculated values of $\rho^I(0)$ and $\rho^{II}(0)$. The isomer shift calibration constant obtained is in the range of accepted values and very close to the values reported by Callaway *et al* [12] (-0.17 au mm s⁻¹) and Wakoh and Yamashita [13] (-0.19 au mm s⁻¹).

From Wandji *et al* [7], the difference between the isomer shifts for Fe I and Fe II site is mainly due to the 4s contribution, implying that the electron charge density of 4s electrons at the iron nuclei of the Fe I site is greater than that at the iron nuclei of the Fe II site because of the difference in the Fe-Si distances. Accordingly, the 4s contribution to isomer shift is very important in determining the isomer shift. However, in addition to the effect of the s orbitals directly influencing the isomer shift, it should be noted that 3d screening effects indirectly influencing the electron charge densities at iron nuclei through the screening of the 3s and 4s electrons play very important roles in determining the isomer shift. Hence it is essential to evaluate the number of 3d electrons for both clusters so as to estimate the 3d screening effect quantitatively.

The number of electrons occupying the 3d orbitals is calculated by Mulliken's [14] method. On the basis of Mulliken's idea, the number of electrons occupying orbital i , namely the orbital population n_i , is defined as

$$n_i = \sum_m \sum_j C_{mi} C_{mj} S_{ij} \quad (3)$$

where S_{ij} is the overlap integral between the atomic orbitals χ_i and χ_j and is expressed as

$$S_{ij} = \langle \chi_i | \chi_j \rangle \quad (4)$$

and C_{ni} are variational coefficients; each molecular orbitals $\Psi_n(\mathbf{r})$ is expressed as the summation of the product of atomic orbital $\chi_i(\mathbf{r})$ and C_{ni} on the basis of MO LCAO theory:

$$\Psi_n(\mathbf{r}) = \sum_i C_{ni} \chi_i(\mathbf{r}). \quad (5)$$

Table 2 shows the orbital populations of the 3d orbitals ($|3z^2 - r^2\rangle$, $|x^2 - y^2\rangle$ and $|xy\rangle$, $|xz\rangle$, $|yz\rangle$) for the Fe^ISi₈ and Fe^{II}Si₈ clusters. Then the n_d of 3d electrons for the Fe^ISi₈ and Fe^{II}Si₈ clusters are 6.39 and 6.55, respectively.

Table 2. Calculated orbital populations of 3d orbitals for Fe^ISi₈ and Fe^{II}Si₈ clusters.

	$ 3z^2 - r^2\rangle$	$ x^2 - y^2\rangle$	$ xy\rangle$	$ xz\rangle$	$ yz\rangle$
Fe ^I Si ₈ cluster	0.957	0.398	1.905	1.920	1.208
Fe ^{II} Si ₈ cluster	1.713	1.383	1.373	1.327	0.755

Mulliken's population analysis, as stated above, shows that the number of 3d electrons in the Fe^{II}Si₈ cluster is greater than that in the Fe^ISi₈ cluster. Considering that the screening effect by 3d electrons is proportional to the number of 3d electrons, the screening effect in the Fe II site is assumed to be greater than in the Fe I site, consequently causing a greater decrease in the s electron charge densities at the Fe II site. Accordingly, the possibility of increase in the isomer shift in the Fe II site by the 3d screening effect should be considered.

Combining the report of Wandji *et al* [7] with the above calculated results, we could conclude, therefore, that the difference between the isomer shifts of the two sites is ascribed to the contribution of 4s electron and the screening effect caused by 3d electrons.

3.2. Dependence of the isomer shift on Co dopant concentration in β -FeSi₂

Figure 2 illustrates the isomer shifts of both Fe sites (Fe I site and Fe II site) in Fe_{30-x}Co_xSi₇₀ alloy. As shown in figure 2, the isomer shifts of the two sites are found to be dependent upon the Co dopant concentration in β -FeSi₂; the isomer shifts for both sites increase with increasing Co concentration. Accordingly, Co atoms are found to enhance the isomer shift. It is, therefore, essential to clarify how Co atoms exist in β -FeSi₂, so as to investigate the effect of Co atoms on isomer shifts in detail.

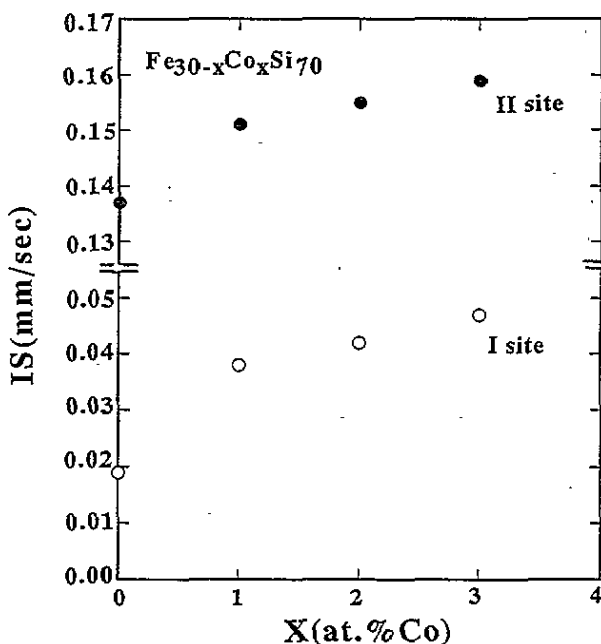


Figure 2. Isomer shifts of Fe I and Fe II sites in Fe_{30-x}Co_xSi₇₀ alloys.

Since the atomic size of the Co atom is about the same as that of Fe and is greater than that of Si, there seems little possibility that Co atoms occupy the interstitial site in the lattice of β -FeSi₂ in the light of the atomic size. Consequently Co atoms are assumed to occupy Si sites and/or Fe sites (Fe I and Fe II sites). From the analysis by atom location by channelling-enhanced microanalysis (ALCHEMI) [15] Co atoms are proved to occupy not Si sites but Fe sites. Further analysis of the Mössbauer spectrum shows that Co atoms occupy

Fe II sites preferentially [8]. Therefore, we can conclude that Co atoms occupy the Fe II site.

Table 3 shows the atomic distances in each Fe site. As illustrated in table 3, the Fe-Si distances vary from 0.234 to 0.239 nm for the Fe I site and from 0.233 to 0.244 nm for the Fe II site. The nearest atomic distance from the Fe I site to the Fe II site is 0.297 nm and from the Fe II site to another Fe II site is 0.402 nm. Accordingly, considering that Co atoms occupy Fe II sites preferentially, the nearest atomic distance of Co to the Fe I site is 0.297 nm and of Co to the Fe II site is 0.402 nm; thereby the influence of Co atoms on $\rho(0)$ in the Fe II sites seems very small in the light of the atomic distance. As a result, only the change in the isomer shift of the Fe I site can be expected on the basis of the above discussion; however, this appears inconsistent with the experimental result of the increase in both isomer shifts. Hence the idea that the isomer shifts of Co-doped β -FeSi₂ could be interpreted on the basis of Co-Fe atomic distances cannot explain the increase in isomer shifts of both Fe sites as shown in figure 2. Therefore, we should abandon the above assumption and seek another reason to explain the experimental results.

Table 3. Atomic distances for Fe I and Fe II sites, where Si I and Si II means Si I and Si II sites, respectively.

X	Fe I site r (Fe I-X) (nm)	X	Fe II site r (Fe II-X) (nm)
Si I	0.2338	Si I	0.2437
Si I	0.2338	Si I	0.2437
Si I	0.2376	Si I	0.2333
Si I	0.2376	Si I	0.2333
Si II	0.2385	Si II	0.2429
Si II	0.2385	Si II	0.2429
Si II	0.2339	Si II	0.2335
Si II	0.2339	Si II	0.2335
Fe I	0.3957	Fe I	0.2967
Fe I	0.3957	Fe I	0.2967
Fe I	0.3978	Fe I	0.3975
Fe I	0.3978	Fe I	0.3975
Fe II	0.2967	Fe II	0.4022
Fe II	0.2967	Fe II	0.4022
Fe II	0.3975	Fe II	0.4027
Fe II	0.3975	Fe II	0.4027

Since a change in lattice parameter due to the Co dopant is expected in the specimen, we assume that the change in lattice parameter has an influence on the isomer shifts. The relation between the atomic distance such as the iron-ligand distance and isomer shifts has been reported and discussed experimentally and/or theoretically [16-18]; isomer shifts are found to be very sensitive to the atomic distance. Since the change in lattice parameter causes the change in Fe-Si distances, our assumption relating the lattice parameter to the isomer shifts appears reasonable.

However, the crystalline structure of β -FeSi₂ is, as stated previously, very complex and both clusters (Fe^ISi₈ and Fe^{II}Si₈ clusters) from which the crystalline structure is constructed are low symmetry with slightly different Fe-Si distances. Hence we could not specify an accurate Fe-Si distance for both clusters and the mean Fe-Si distance seems insufficient and/or ineffective for clusters with low symmetry. Then, instead of introducing a mean

Fe–Si distance, we introduce the scaling ratio k with no dimension into both clusters, which is defined as follows:

$$r_j = kr_j^0 \quad (j = 1, 2, \dots, 8) \quad (6)$$

where the subscript j indicates the j th Si atom in the Fe^ISi₈ or Fe^{II}Si₈ cluster; j varies, as illustrated in equation (6), from 1 to 8 because of the presence of eight Si atoms in each cluster. Figure 3 shows this transformation schematically. r_j^0 is the vector from the Fe atom to each Si atom before transformation. Since $r_i \cdot r_j / r_i r_j = r_i^0 \cdot r_j^0 / r_i^0 r_j^0$ for all i, j ($i, j = 1, 2, \dots, 8$), the angle of the i th Si through Fe to the j th Si remains constant by this transformation. Consequently, such a transformation as proposed in equation (6) means a similar transformation with no deformation in the shapes of both clusters, changing only the Fe–Si distance. Also, as shown in figure 3 and equation (6), the Fe–Si distance increases when $k > 1$, whereas it decreases when $k < 1$.

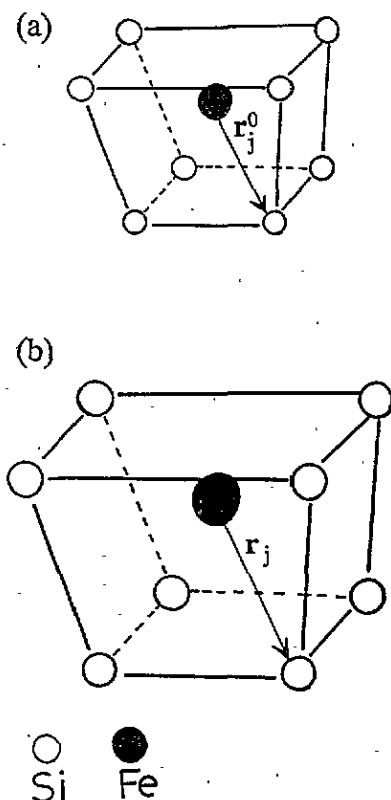


Figure 3. Illustration describing the transformation as shown in equation (6): (a) crystalline structure before transformation; (b) crystalline structure after transformation when the scaling ratio $k > 1$ (isotropic expansion).

Figure 4 illustrates the relation between the scaling ratio k and $\rho(0)$ for both clusters. The electron charge densities for both clusters tend to decrease with increase in k . Consequently the increase in the Fe–Si distance results in a decrease in $\rho(0)$, thus increasing

the isomer shifts of both Fe sites. It is, therefore, concluded that the increase in the isomer shifts of both Fe sites as found in figure 2 is ascribed to the increase in Fe-Si atomic distances; the dependence of the isomer shifts for both Fe sites on Co concentration can be interpreted as the dependence of the lattice parameter of β -FeSi₂ on Co concentration.

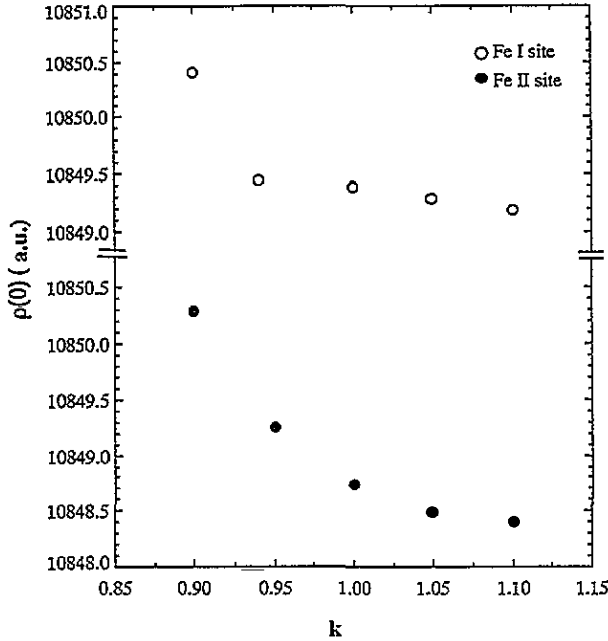


Figure 4. Relation between the scaling ratio k and electron charge densities $\rho(0)$ at iron nuclei for Fe I and Fe II sites.

Although the decrease in $\rho(0)$ with increase in Fe-Si distance is observed, the rates of decrease, namely $d\rho(0)/dk$, are not the same for both Fe sites. $d\rho(0)/dk$ -values for Fe I and Fe II sites are about -2.1 au and -3.3 au, respectively when $k > 1$. Accordingly, if we assume the isomer shift calibration constant α to be -0.18 au mm s^{-1} , the calculated isomer shifts for the Fe I and Fe II sites are $+0.039$ mm s^{-1} and $+0.183$ mm s^{-1} , respectively when $k = 1.05$. However, the isomer shift obtained experimentally is $+0.038$ mm s^{-1} for the Fe I site and $+0.151$ mm s^{-1} for the Fe II site in the $\text{Fe}_{29}\text{Co}_1\text{Si}_{70}$ alloy; thus the isomer shift calculated for the Fe II site appears too large in comparison with the observed data.

As stated previously, β -FeSi₂ belongs to the orthorhombic system with $a = 0.9863$ nm, $b = 0.7791$ nm and $c = 0.7833$ nm. Since the isotropic deformation of a , b and c axes into $(1 + \epsilon)a$, $(1 + \epsilon)b$ and $(1 + \epsilon)c$ corresponds to the transformation of $k = 1 + \epsilon$ as described in equation (6), such a transformation as stated in equation (6), therefore, means the isotropic transformation of the crystalline lattice with uniform expansion or contraction of the a , b and c axes. However, on the assumption of the isotropic transformation in β -FeSi₂, the isomer shift calculated for the Fe II site, as pointed out previously, results in a large value, compared with the observed isomer shift. Thereby the lattice expansion in β -FeSi₂ caused by Co doping is assumed to be an anisotropic transformation. From the analysis on x-ray diffraction for Co-doped β -FeSi₂, expansion of the a axis has been

reported [3]; this experimental result seems to support the idea of anisotropic expansion of the lattice.

3.3. Isomer shift for another transition-metal (Mn or Ni)-doped β -FeSi₂

Figure 5 illustrates the isomer shifts of the Fe I and Fe II sites in Fe₂₈M₂Si₇₀ alloy (M = Mn, Fe, Co or Ni). The isomer shifts of both iron sites in Mn- or Ni-doped β -FeSi₂ are large, compared with those in undoped β -FeSi₂. Since the analysis of Mössbauer effects indicates that Ni atoms occupy Fe II sites [11] whereas Mn atoms occupy Fe I sites [8], this increase in isomer shifts for both Fe sites is, as discussed in the previous paragraph, assumed to be mainly due to the lattice expansion caused by the doping element. However, if we assume the lattice expansion to be isotropic, the isomer shift calculated for the Fe II site (= 0.183 mm s⁻¹ when $k = 1.05$) results in a larger value than found experimentally. Consequently the lattice expansion in Mn- or Ni-doped β -FeSi₂ is also assumed to be anisotropic as it is restricted to the expansion of the a , b or c axis.

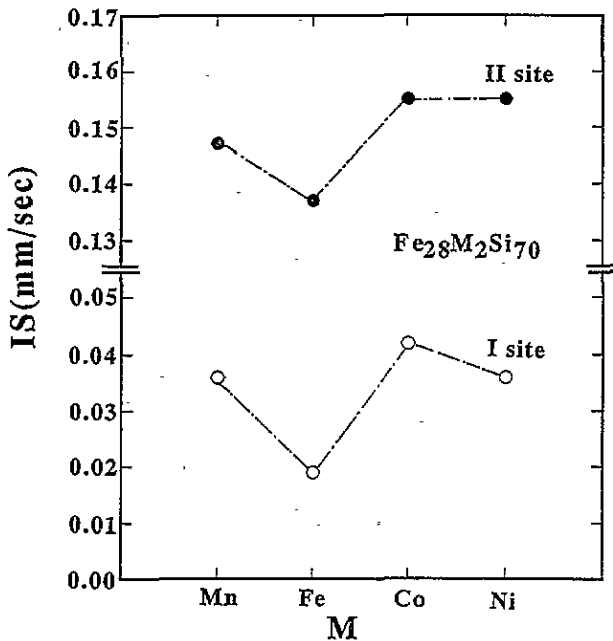


Figure 5. Isomer shifts of Fe I and Fe II sites in Fe₂₈M₂Si₇₀ (M = Mn, Fe, Co or Ni) alloys.

4. Conclusion

From the LCAO SCF cluster calculation, it is found that the calculated electron charge densities $\rho(0)$ at Fe nuclei corresponding to two Fe sites are consistent with the isomer shifts of two Fe sites as experimentally obtained in the Mössbauer spectra of β -FeSi₂. The isomer shift calibration constant α is -0.18 au mm s⁻¹, which is in the range of the accepted values. From the report of Wandji *et al* [7], the difference between the isomer shifts for the two

Fe sites (Fe I and Fe II sites) is mainly assumed to be due to the difference between the Fe-Si distances, which strongly influences the 4s electron charge density. From Mulliken's [14] population analysis, it is found that the number of 3d electrons in the Fe II site is greater than in the Fe I site. Considering that the screening effect caused by 3d electrons is proportional to the number of 3d electrons, the 3d screening effect upon the isomer shifts of the Fe II site appears large in comparison with that upon the isomer shift of the Fe I site, thus decreasing $\rho(0)$ in the Fe II site. In fact both the difference in the Fe-Si distances and the 3d screening effects are assumed to play an important role in determining the isomer shifts of both Fe sites.

A dependence of the isomer shifts of both Fe sites upon the concentration of Co as doped in β -FeSi₂ is observed. Considering that Co atoms occupy Fe II sites preferentially, it seems difficult to explain the increase in isomer shift in the Fe II site in the light of the atomic distance of the Co site to the Fe II site. Hence the influence of the change in lattice parameter should be considered; the isomer shifts of both Fe sites were found to be strongly dependent upon the lattice parameter, increasing with lattice expansion. Accordingly it is concluded that the increase in both isomer shifts is attributable to the lattice expansion of β -FeSi₂ due to the Co dopant. Although the change in lattice parameter strongly influences the isomer shift, the dependence of $\rho(0)$ upon the lattice parameter is different in the two clusters (Fe^ISi₈ and Fe^{II}Si₈). On the assumption that the lattice expansion is isotropic, the isomer shift calculated for the Fe II site is too large, compared with observed data. This implies that the lattice expansion due to the Co dopant is not isotropic but anisotropic.

An increase in the isomer shifts of other transition-metal (Ni or Mn)-doped β -FeSi₂ was observed; this is also interpreted as due to the expansion of lattice caused by the doping element on the basis of the above discussion.

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