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Abstract. The valence hyperfine fields of atoms in fcc iron and nickel containing 2p interstitials X (X = B, C, N, O and F) have been investigated by applying the spin-polarized LMTO method. The results on the valence hyperfine field and the hyperfine coupling constants indicate that the Fe–Fe and Ni–Ni interactions are sensitively dependent on which interstitial atom is present, and also that Fe–X interactions dominated by bonding states are distinguishable from those between Ni and X atoms which 'prefer' anti-bonding states. The volume (distance) dependences of the valence hyperfine fields in Fe–X are also investigated, and the results reveal an anomalous distance dependence of the three hyperfine coupling constants. It is concluded that it is the unusual distance dependence of the strong interactions between face-centred Fe and X atoms that gives rise to these anomalies.

1. Introduction

The hyperfine field at the nucleus, which can be detected by nuclear methods, is a very important characteristic parameter for the understanding of local electronic and magnetic properties of magnetic systems. During the past decade, much progress has been made in theoretical studies of the hyperfine field in ferromagnetic metals and alloys [1, 2].

In 3d-transition-metal alloys and compounds with cubic symmetry, the Fermi-contact term (H_{FC}) provides the main contribution to the hyperfine field H_{hf} of an atom, and H_{FC} is closely related to the local magnetism. It can be decomposed into core (H_{FC}^{core}) and valence (H_{FC}^{val}) contributions. The former comes from the polarization of the core electrons and is proportional to the local magnetic moment of the atom; the latter stems from the conduction electron polarization. Although normally it only constitutes a small contribution to H_{FC} for a magnetic atom, H_{FC}^{val} is very important to the understanding of the local electronic and magnetic properties of a system due to its sensitivity to the neighbouring environments and to the interactions with neighbours. In particular, the hyperfine field at non-metallic interstitial atoms in a crystal comes mainly from the transferred contribution of magnetic atoms. Recently, theoretical and experimental investigations [3, 4] on transition metal nitrides have suggested that the transferred hyperfine field plays an important role when the volume (pressure) dependence of the total hyperfine field at the Fe atom is considered. The results calculated for $(Fe_{1-x}Ni_x)_4N$ [5] have revealed an anomalous dependence of the transferred field at the nitrogen atom on the interatomic distance. All of these findings suggest that further studies are required if we are to thoroughly understand the hyperfine field in transition metal alloys and compounds.

In the past, Takeda *et al* [6] studied the hyperfine field of light interstitials in bcc Fe. Coey and Qi [7] have published some valuable results on 2p interstitials in Fe but no further discussion has been given. Our previous publication [8] reported on calculations for Fe_4Z (Z = H, C and N), and the results indicated that the hyperfine fields of Z atoms depend sensitively upon the Fe–Z interactions. In the present study we use the self-consistent LMTO method to calculate the valence hyperfine field in fcc Fe and Ni with 2p interstitials at the body-centred octahedral interstitial sites, indicated as Fe–X and Ni–X where X denotes the 2p interstitial atoms B, C, N, O and F, and try to present a reliable picture of the relation of the hyperfine field to the local magnetic properties of the transition metal compounds. It is noted that the lattice structure studied is the same as that of ferromagnetic γ'-Fe_4N. So this study may be considered as a continuation of our study on transition metal nitrides.

In section 2 we will briefly describe the LMTO method, the details of the calculation and the results on the hyperfine fields at each of the lattice sites. The results calculated are further discussed in the next section. Some concluding remarks are included in the last section.

2. Computational parameters and calculated results

Using the LMTO method that is described in references [9, 10], we have performed a semi-relativistic spin-polarized band calculation on fcc Fe and Ni containing the light interstitial atoms B, C, N, O and F at octahedral body-centred sites. In our calculation, the exchange–correlation term is introduced in the form deduced by von Barth and Hedin [11]. The Brillouin-zone integration is carried out for 286 k-points in the irreducible zone. We use partial waves up to $l = 2$ for the valence electrons of Fe and Ni, which are 3d, 4s electrons, and apply s, p orbitals for the 2s, 2p electrons of interstitials. We deem convergence to be achieved when the root mean square error of the self-consistent potential is smaller than 0.5 mRyd.

When an interstitial atom is introduced at a body-centred site of an fcc lattice, as mentioned above, the resulting lattice geometry is the same as that of γ'-Fe_4N [12]. In the unit cell, two inequivalent crystallographic sites, the corner (c) and the face-centred (f) sites, are produced. An atom at a c site is surrounded by 12 nearest-neighbouring atoms at f sites, while an atom at an f site has two interstitial atoms as nearest neighbours, and four and eight atoms at c and f sites, respectively, as next-nearest neighbours. In our calculations we use the same value for the atomic radii of the metal atoms at the two sites, and for all of the interstitial atoms the ratios of their covalent radii to those of Fe and Ni atoms are taken to determine the atomic radius S_i assigned in the atomic-sphere approximation (ASA).

It should be pointed out that in our study a self-consistent determination of the lattice relaxation is not included. We introduced the same lattice expansion with respect to the lattice dimension of stable γ'-Fe_4N in all of the cases that we studied. To observe the influence of lattice relaxation on the hyperfine field, we also performed the calculations on Fe–X with various lattice spacings. Using the results calculated for the electronic structure, we calculate the Fermi-contact hyperfine field at individual sites in Fe–X and Ni–X according to the prescription from Akai *et al* [1]. In spite of there being a core contribution, which is simply proportional to the on-site local magnetic moment, we concentrate on the valence hyperfine field H_{FC}^{val}. The value of H_{FC}^{val} can be calculated by summing the valence charge densities at the nuclei, and the results are presented in table 1 together with the on-site magnetic moments. Since some electronic structure parameters, such as the charge transfer and charge densities at nuclei, are highly sensitive to the radius of the atomic sphere present, we immediately notice that the values of H_{FC}^{val} at Fe, N and C sites in Fe–N and Fe–C are

Table 1. The calculated valence hyperfine fields (kG) and total magnetic moments (μ_B) in Fe–X and Ni–X.

	X:	B	C	N	O	F
Fe^c	H_{FC}^{val}	3.8	27.6	−50.6	−61.3	136.8
	μ_{total}	3.17	3.25	3.14	3.02	3.69
Fe^f	H_{FC}^{val}	−61.5	−72.3	−37.9	−92.7	−35.5
	μ_{total}	1.90	1.60	2.16	2.24	0.69
X	H_{FC}^{val}	−22.3	−28.0	−59.3	−92.2	−9.0
	μ_{total}	−0.12	−0.08	0.0	0.03	−0.01
Ni^c	H_{FC}^{val}	71.3	46.0	21.3	20.2	30.0
	μ_{total}	0.88	1.00	0.99	0.90	0.81
Ni^f	H_{FC}^{val}	−17.1	23.1	18.0	−22.3	−12.9
	μ_{total}	0.07	0.23	0.32	0.25	0.54
X	H_{FC}^{val}	11.9	20.5	26.6	47.7	142.2
	μ_{total}	0.008	0.04	0.03	0.02	0.03

different from the previous calculated results [8] due to the different choice made for the ratio of the atomic radii, $p = S_X/S_{Fe}$. However, the quantitative difference caused by the different choice of parameters does not affect our present analysis.

3. Discussion

The valence hyperfine field consists of two parts; one is the local valence contribution $H_{FC}^{val,L}$ which is proportional to the local s magnetic moment and the other is called the transferred hyperfine field $H_{FC}^{val,T}$ which is the result of sd hybridization between the s orbitals of the on-site atom and the spin-polarized d orbitals of its neighbouring magnetic atoms. For several years, the intrinsic relation between the transferred term arising from the neighbours and the local magnetic properties has attracted much attention and many models have been provided [13]. It is suggested that the hyperfine field is connected to the local magnetic moment of the on-site atom and to those of its neighbours by hyperfine coupling constants. According to the description given by Akai *et al* [1] and Zhang *et al* [14], the valence hyperfine field of the i-atom can be expressed as

$$H_{FC}^{val}(i) = A\mu_s(i) + \sum_j D_{ij}n_{ij}\mu(j) \tag{1}$$

where $\mu_s(i)$ is the on-site s magnetic moment of the i-atom, n_{ij} and $\mu(j)$ are the number and the moment of the neighbouring j-site magnetic atom, and A and D_{ij} are hyperfine coupling constants. Normally, A is a constant for atoms at each site in the same system but the D_{ij} are site dependent. Since the local s magnetic moments of the atoms at all three sites in Fe–X and Ni–X are very small, neglecting the minor local valence term in H_{FC}^{val} we assign the considerable valence hyperfine field completely to the transferred contribution from the magnetic neighbours. Considering only the effects of magnetic nearest neighbours, we can further write H_{FC}^{val} at all three sites as follows:

$$H_c^{val} = 12D_{cf}\mu_f \tag{2}$$
$$H_f^{val} = 4D_{fc}\mu_c + 8D_{ff}\mu_f \tag{3}$$

and

$$H_X^{\text{val}} = 6D_{\text{Xf}}\mu_{\text{f}}. \tag{4}$$

Since the neighbour distance between atoms at c and f sites is identical to that between atoms at f sites, $H_{\text{c}}^{\text{val}}$ comes from the sd hybridization of the atoms at c sites with their 12 nearest-neighbour atoms at f sites, but $H_{\text{f}}^{\text{val}}$ is simultaneously contributed by four atoms at c sites and eight atoms at f sites. Also, the site dependence of the three coupling constants (D_{cf}, D_{fc} and D_{ff}) simply results from the different interactions between atoms at the two sites. The relation $D_{\text{cf}} = D_{\text{fc}}$ should hold for the same system.

3.1. The valence hyperfine field of Fe and Ni

As concluded in a previous publication [8], the strong Fe$^{\text{f}}$–X interactions affect the interactions between Fe atoms. As a consequence, $H_{\text{FC}}^{\text{val}}$ for Fe (Ni) in Fe (Ni)–X is not only related to which interstitial X atom is present, but is also site dependent. From the results listed in table 1, this can be clearly seen. Moreover, $H_{\text{FC}}^{\text{val}}$ for Ni in Ni–X is also different from that for Fe for the same interstitial atom. In particular, in Fe–N, $H_{\text{FC}}^{\text{val}}$ is negative at both Fe sites, while for Ni in Ni–N it is positive, which indicates a substantial difference between Ni–Ni and Fe–Fe interactions.
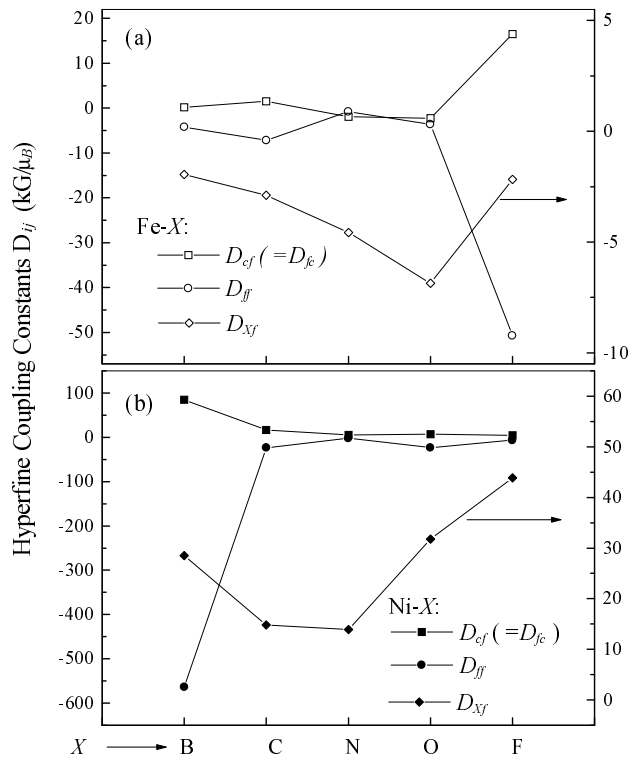
Figure 1. The calculated hyperfine coupling constants D_{ij} for (a) Fe–X and (b) Ni–X.

Generally speaking, the bonding states induced by sd hybridization produce a negative contribution to $H_{\text{FC}}^{\text{val}}$ while the anti-bonding states lead to a positive contribution to $H_{\text{FC}}^{\text{val}}$. In order to clarify the difference of these interactions, using expressions (2) and (3) we

have derived the hyperfine coupling constants D_{cf} and D_{ff} for Fe–X and Ni–X; we have illustrated these in figure 1. It can be seen that, on the whole, D_{cf} and D_{ff} are larger for Ni–X than for Fe–X. It is suggested that the larger number of d electrons in Ni have enhanced the sd hybridization, resulting a larger specific spin polarization of valence s electrons at the nucleus, in spite of the magnetic moment of Ni being smaller than that of Fe. In particular, for Ni–B, the much larger value of D_{ff} must be responsible for the comparable value of H_{FC}^{val} for Ni^f, where the moment of its Ni^f neighbour is only $0.07\mu_B$. For Ni–X, D_{cf} remains positive from B to F, but the values of D_{ff} are all negative. Because the magnetic moments of Ni are all positive, it is concluded that anti-bonding states dominate the Ni^c–Ni^f interactions leading to a positive spin polarization of the s valence electron at the nucleus, while a negative valence s polarization at the f site is induced by bonding states in Ni^f–Ni^f interactions. With increasing atomic number of the interstitial atom, D_{cf} and D_{ff} for Ni–X have a tendency to decrease in value. For Fe–X, the positive D_{cf} and the negative D_{ff} for B, C and F interstitials have indicated similar hybridization interactions between Fe atoms to those in Ni–X, but this tendency does not hold for Fe–N and Fe–O, where D_{cf} and D_{ff} are always negative; thus, the interactions between these Fe atoms is entirely governed by bonding states. Moreover, it is interesting to note that the largest difference between D_{cf} and D_{ff} is shown for Ni–B, but for Fe–X this occurs in the case of Fe–F. With the assumption that the difference of D_{cf} and D_{ff} is caused by strong Fe^f (Ni^f)–X interactions, this observation implies that the Fe^f–F and Ni^f–B interactions are the strongest ones among those in Fe–X and Ni–X, respectively.

The valence hyperfine field is also distance dependent. On the basis of their NMR results on Y–Co compounds, Figiel *et al* [15] suggested that the dependence of the transferred hyperfine field on the neighbour distance can be described by the expression

$$H_{hf} = \alpha' \sum_i \frac{N_i}{r_i^n} \mu_i \qquad (5)$$

where r_i is the distance to the neighbour atom and α' is regarded as a constant parameter for the system. For the system studied below, we can investigate the distance dependence of H_{FC}^{val} at each site by changing the lattice relaxation produced by the interstitial atoms.

Table 2. The calculated spin-polarized s charge density (au^{-3}) at nuclei in Fe–X, with the lattice parameters $a = 0.3797$ and 0.3597 nm.

| X:	B	C	N	O	F
$a = 0.3597$ nm			$\rho_s(\uparrow/\downarrow)$		
Fe^c	3.952/3.671	3.803/3.543	3.759/3.557	3.700/3.614	3.020/2.753
Fe^f	3.701/3.831	3.493/3.628	3.264/3.417	3.109/3.285	4.555/4.637
X	0.959/0.953	1.844/1.833	3.448/3.446	5.818/5.868	3.732/3.728
$a = 0.3797$ nm			$\rho_s(\uparrow/\downarrow)$		
Fe^c	3.303/3.296	3.188/3.136	3.113/3.210	3.110/3.227	2.548/2.287
Fe^f	3.170/3.287	2.921/3.059	2.824/2.896	2.631/2.808	3.708/3.776
X	0.860/0.903	1.757/1.810	3.332/3.445	5.560/5.736	3.318/3.335

In figure 2 we have presented H_{FC}^{val} calculated for Fe atoms at both sites in Fe–X as a function of the lattice volume. To help in achieving a good understanding of the change of H_{FC}^{val} with volume, additionally the spin-polarized s charge densities ρ_s at the nuclei for two chosen volumes have been listed in table 2. Here the p and d densities are omitted
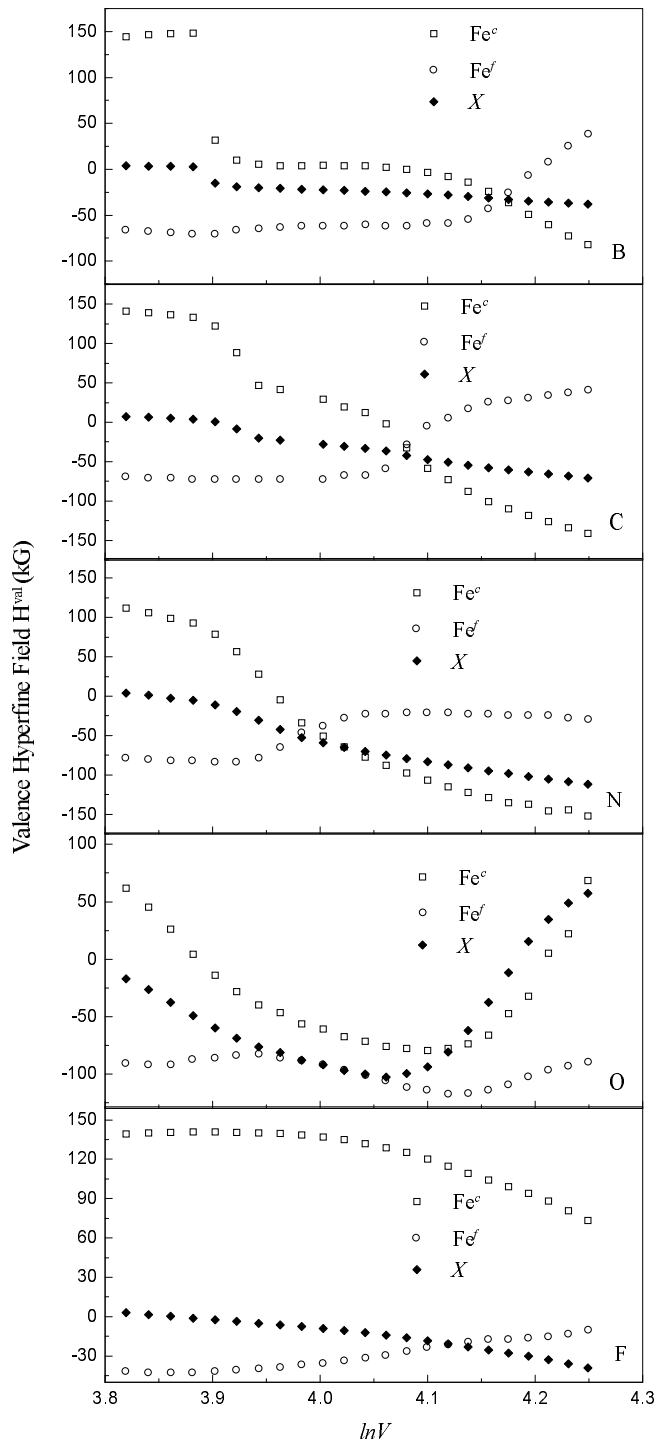
Figure 2. The valence hyperfine field H_{FC}^{val} of atoms in Fe–X as a function of the volume.

since they are of the order of 10^{-5} and 10^{-11}, respectively, of the value of ρ_s. For all Fe–X except Fe–O, H_c^{val} and H_f^{val} show quite different lattice volume dependences. H_c^{val} is positive on the low-lattice-dimension side and decreases markedly with increasing lattice spacing, whereas simultaneously H_f^{val} is negative, showing a continuous increase. For Fe–B and Fe–C the volume dependences are much larger; H_c^{val} and H_f^{val} have already reversed in sign on the large-volume side. Moreover, H_c^{val} exhibits an additional abrupt decrease on the low-volume side for Fe–B, Fe–C and Fe–N. The most complex volume dependences are observed in Fe–O, for which H_c^{val} and H_f^{val} exhibit pronounced minima in the intermediate-volume region.
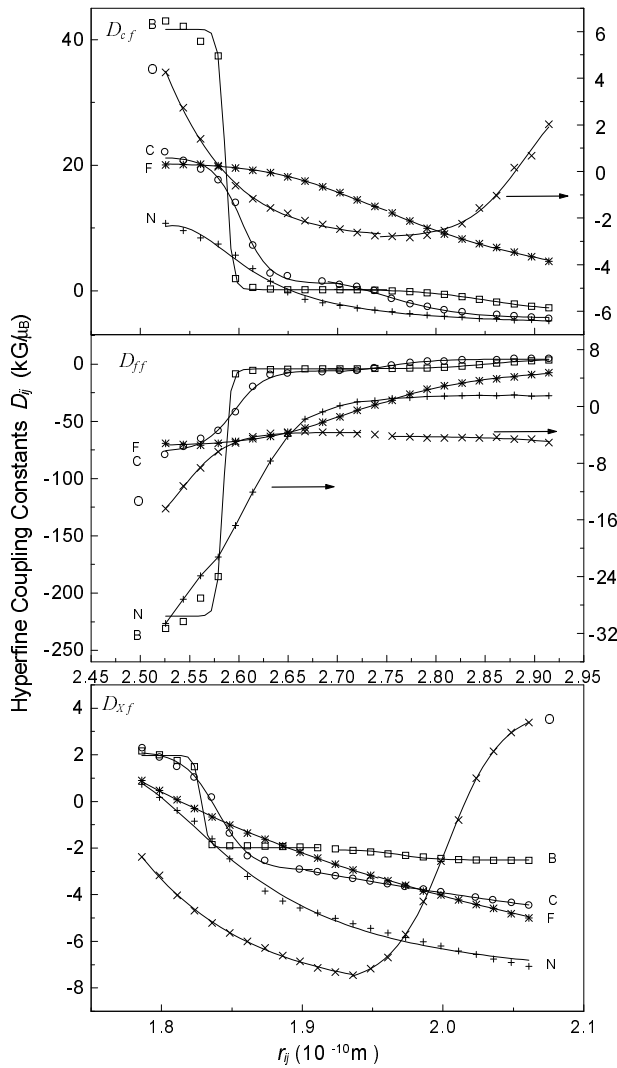
Figure 3. The distance dependence of the hyperfine coupling constants D_{ij} for Fe–X.

According to expressions (1) and (5), the anomalous features in the distance dependence of H_c^{val} and H_f^{val} might be well explained by the changes of neighbour magnetic moments and corresponding hyperfine coupling constants with lattice volume. The former is the

volume dependence of a local magnetic property, while the latter is related to the changes of interactions between atoms with lattice spacing. From the calculated electronic structure, it has been indicated that the magnetic moments at c and f sites in Fe–X increase with lattice volume, and that the moment at the c site is much more stable against the change of volume. So the anomalous volume dependences of H_c^{val} and H_f^{val} must be resulting from the distance dependence of the coupling constants D_{cf} and D_{ff}, i.e. interactions among atoms. In general, interaction at larger distances produces a weaker hyperfine coupling between atoms, leading to a smaller transferred hyperfine field when the neighbour magnetic moment remains constant. But in Fe–X the strong Fe^f–X interaction causes deviation from this simple behaviour [8]. By subtracting the contribution from the neighbour distance dependence of the neighbour magnetic moments, the coupling constants D_{cf} and D_{ff} in Fe–X can be derived for various lattice spacings; the results are illustrated in figure 3. For all interstitial atoms, quite opposite distance dependences of D_{cf} and D_{ff} are found. For Fe–B, Fe–C and Fe–N, D_{cf} and D_{ff} show similar distance dependences. Because it relates to small distances, a jump of D_{cf} to a lower value leads to a large reduction of H_c^{val}, and the jump in D_{cf} has partly compensated for the influence of a similar abrupt change of D_{ff}, which has the opposite sign, on H_f^{val}. On increasing the neighbour distance further, the magnitudes of D_{cf} and D_{ff} reduce continuously and their sign gets reversed first for N, then for C and then for B. As a consequence, H_c^{val} and H_f^{val} for Fe–B and Fe–C also reverse in sign on the larger-distance side. The distance dependences of D_{cf} and D_{ff} for Fe–B, Fe–C and Fe–N suggest that the change of Fe^c–Fe^f (Fe^f–Fe^f) interactions is accompanied by a reduction of the positive (negative) spin polarization of the conduction electron at the corresponding nucleus, which has been seen in table 2, and a change of the polarization direction with the further increase of the distance. D_{cf} and D_{ff} for Fe–F change in a similar way with the neighbour distance, but the abrupt jump and the sign reversal are lacking. Extrapolation of D_{cf} and D_{ff} for Fe–F to larger distances yields an indication of a possible sign reversal. For Fe–O, the parabola-like distance dependence of D_{cf} indicates a more complex variation of the Fe^c–Fe^f interactions. With increasing distance, D_{cf} changes its sign twice, while no sign reversal occurs for D_{ff}; their combined contribution causes H_f^{val} to show an oscillating distance dependence.

In summary, these unusual distance dependences of D_{cf} and D_{ff} reveal large effects of interstitial atoms on Fe–Fe interactions. It might be suggested that the sign reversal of the spin polarization of the conduction electron and—especially—the abrupt jump of D_{cf} and D_{ff} at small distances are dominated by the strong Fe^f–X interactions. This has been confirmed in the discussion of the hyperfine field of interstitial atoms. Moreover, it has been found that it is very difficult to construct a unique analytical expression relating D_{cf} and D_{ff} to the distance r. Although two Boltzmann-type functions fitted the distance dependence of D_{cf} and D_{ff} well on the small- and large-distance sides, respectively, the physical implications are not yet clear.

3.2. The valence hyperfine field of the interstitial atoms

As suggested above, it is the unusual distance dependence of Fe–X interactions that produces the anomalous distance dependence of the coupling constants D_{cf} and D_{ff}. Therefore, it is of interest to investigate the valence hyperfine field of the interstitial X atom in more detail.

The H_{FC}^{val}-values of the interstitial X atoms in Fe–X and Ni–X have been listed in table 1. First of all, the calculated data clearly indicate that H_{FC}^{val} for X atoms depends sensitively upon which coordinated metal atom is present and that the Ni–X interactions are totally different from those of the Fe–X interactions. All of the interstitial atoms in Ni–X have

positive H_{FC}^{val}, which implies that the Ni^f–X hybridizations are dominated by anti-bonding states and produce a positive spin polarization at the X nucleus. On the other hand, the bonding states are favoured by Fe^f–X interactions, and an induced negative spin polarization at an X nucleus should give rise to a negative contribution to H_{FC}^{val} for all X atoms. This is in agreement with the suggestion made in the previous study for $(Fe_{1-x}Ni_x)_4N$ [5], where H_{FC}^{val} for N is dominated by the bonding states for low Ni content and by the anti-bonding states at high Ni content. Moreover, the difference in H_{FC}^{val} for X atoms, which is induced by different Fe^f (Ni^f)–X interactions, has been clearly manifested in figure 1 by the behaviour of the hyperfine coupling constant D_{Xf}. For Fe–X, D_{Xf} tends to increase in value in the sequence from B to O, suggesting a larger negative spin polarization at the X nucleus produced by more bonding states for Fe^f and X atoms. Meanwhile, an increase in the number of anti-bonding states of Fe^f and F has reduced the negative spin polarization at the F nucleus, suggesting a saturation of the bonding states of Fe^f and X with increasing number of X valence electrons. D_{Xf} for Ni–X indicates a similar tendency of Ni^f–X interactions with variation of the X atom, but, because Ni contains more d electrons, such saturations of the bonding states of Ni^f and X occur earlier in Ni–O.

In figure 2, H_{FC}^{val} as a function of the lattice volume calculated for X atoms in Fe–X is also illustrated. With increasing lattice volume, the positive fields H_{FC}^{val} for B, C, N and F decrease monotonically, and have already reversed in sign on the low-volume side. As compared to those for B, C, N and F, H_{FC}^{val} for O exhibits a different lattice volume dependence. It is worth mentioning that, without any exception, the volume dependence of H_{FC}^{val} for an interstitial atom is always similar to that for Fe^c. It may be suggested that the strong Fe^f–X interaction produces a non-negligible effect on the Fe–Fe interactions. This is confirmed by the distance dependence of D_{Xf} for Fe–X, which has been shown in figure 3. In connection with the abrupt changes of D_{cf} and D_{ff} on the small-volume side, it might be suggested that there exists a 'critical distance' in Fe–B, Fe–C and Fe–N. For smaller distances, the Fe–X interactions are dominated by anti-bonding states, while beyond the critical distance, the interactions give preference to bonding states. At the critical distance, the interactions have changed so strongly that an abrupt leap of D_{Xf} occurs for Fe–B and Fe–C. After the reversal of the sign, the further decrease of D_{Xf} for Fe–B, Fe–C, Fe–N and Fe–F with increasing distance reveals the preference given by Fe–X interactions to bonding states at larger distances due to the decrease of the valence electron density. In agreement with the distinct volume dependence of H_{FC}^{val} for O atoms, for larger distances D_{Xf} also behaves differently for Fe–O to in the other cases. This distinctiveness of Fe–O should be assigned to special Fe–O interactions, clarification of which could be expected from investigation of the electronic structure of Fe–O.

4. Conclusions

On the basis of the results on electronic structure calculated by the spin-polarized LMTO method, we have successfully investigated the valence hyperfine field H_{FC}^{val} for metal and interstitial atoms in fcc Fe and fcc Ni, with a light X atom at a body-centred octahedral interstitial position (X = B, C, N, O and F).

The results on the valence hyperfine fields and hyperfine coupling constants for Fe–X and Ni–X have confirmed that the influence of which interstitial atom is present on the Fe–Fe (Ni–Ni) interactions is substantial. The strong interactions between face-centred Fe (Ni) and the interstitials make the Fe–Fe (Ni–Ni) interactions site dependent. Our results have also indicated that the Fe^f–X interactions dominated by bonding states are quite different from the Ni^f–X interactions, in which anti-bonding states are important. The investigation

of the volume (distance) dependences of H_{FC}^{val} and of the coupling constants D_{ij} for Fe–X has revealed an anomalous distance dependence of the interactions between the atoms. In particular, there exists a 'critical distance' for Fe^f–X interactions in Fe–B, Fe–C and Fe–N, at which abrupt reductions of D_{cf} and D_{ff} occur. Among the systems studied, Fe–O displays a distinctive volume (distance) dependence of H_{FC}^{val} and D_{ij}, which could be clarified by the investigation of the electronic structure of Fe–O.

Due to lack of available experimental results on H^{val} for the same or similar systems, we have hardly performed any comparison of our calculated results with measured values. From the ^{57}Fe NMR results [16] on the effective hyperfine field at 4.2 K of γ'-Fe$_4$N and the proportional relation (-130 kG/μ_B) between the core contribution of the hyperfine field and the local magnetic moment, we can derive the valence hyperfine field of Fe at c and f sites indirectly: the values obtained are 18.4 kG and 26.0 kG, respectively. Our calculated absolute results show only poor quantitative agreement. But we expect to compare the calculated changes of H_{FC}^{val} with systematical experimental results in the future.

Acknowledgment

References

[1] Akai H, Akai M, Blügel S, Drittler B, Ebert H, Terakura K, Zeller R and Dederichs P H 1990 *Prog. Theor. Phys. Suppl.* **101** 11 and references therein
[2] Guo G Y and Ebert H 1996 *Phys. Rev.* B **53** 2492
[3] Mohn P, Schwarz K, Mater S and Demazeau G 1992 *Phys. Rev.* B **45** 4000
[4] Yang C L, Abd-Elmeguid M M, Micklitz H, Michels G, Otto J W, Kong Y, Xue D S and Li F S 1995 *J. Magn. Magn. Mater.* **151** L19
[5] Kong Y and Li F S 1998 *Phys. Rev.* B **57** 970
[6] Takeda M, Akai H and Kanamori T 1993 *Hyperfine Interact.* **78** 383
[7] Coey J M D and Qi Q N 1994 *Hyperfine Interact.* **90** 265
[8] Kong Y, Zhou R J and Li F S 1996 *Phys. Rev.* B **54** 5460
[9] Anderson O K 1975 *Phys. Rev.* B **12** 3050
[10] Skriver H L 1984 *The LMTO Method* ed M Cardona, P Fulde and H J Queisser (Berlin: Springer)
[11] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[12] Frazer B C 1958 *Phys. Rev.* **112** 751
[13] Ebert H, Winter H, Johnson D D and Pinski F J 1990 *J. Phys.: Condens. Matter* **2** 443
[14] Zhang Y D, Budnick J I, Ford J C and Hines W A 1991 *J. Magn. Magn. Mater.* **100** 13
[15] Figiel H, Oppelt A, Dormann E and Buschow K H J 1976 *Phys. Status Solidi* a **36** 275
[16] Lord J S, Armitage J G M, Riedi P C, Mater S F and Demazeau G 1994 *J. Phys.: Condens. Matter* **6** 1779