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## Electronic structures and magnetic properties of $\text{Fe}_{16}\text{X}_2$ ( $\text{X} = \text{B}, \text{C}$ and $\text{N}$ )

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**Abstract.** Electronic structures of  $\text{Fe}_{16}\text{X}_2$  ( $\text{X} = \text{B}, \text{C}$  and  $\text{N}$ ) were calculated by the LMTO-ASA method within the framework of the local-spin-density approximation, and the effect of X atoms on the magnetic properties were investigated. The magnetic moments of the Fe(4e) atoms which are nearest to the X atoms decrease. This is due to the hybridization between Fe(4e) d states and X valence states. On the other hand, the Fe(4d) atoms farthest from X atoms carry a very large magnetic moment. The Fe(4d) moment is indirectly influenced by X atoms through the neighbouring Fe and the enhancement increases for  $\text{X} = \text{B}, \text{C}$  and  $\text{N}$ , in that order. The hyperfine fields at Fe(4e) and Fe(8h) in  $\text{Fe}_{16}\text{N}_2$  are nearly equal, though their magnetic moments are different. This fact can be explained on the basis of the difference of the contributions from the valence s electrons.

### 1. Introduction

Kim and Takahashi (1972) reported that a high saturation magnetic flux density was observed for Fe–N film, the high value (2.58 T) being attributed to the formation of  $\text{Fe}_{16}\text{N}_2$ . Since this discovery, the application of  $\text{Fe}_{16}\text{N}_2$  has been awaited. However, it is difficult to prepare a large single crystal. Recently, Komuro *et al* (1990) reported that the single-crystal  $\text{Fe}_{16}\text{N}_2$  films could epitaxially grow onto Fe films, the flux density was estimated as 2.8–3.0 T and the average magnetic moment per Fe was greater than  $2.8\mu_{\text{B}}$ .

It is interesting to investigate theoretically whether or not such giant moments appear on Fe sites and how the moments are changed by substituting B or C for N. We calculate the electronic structures of  $\text{Fe}_{16}\text{X}_2$  ( $\text{X} = \text{B}, \text{C}$  and  $\text{N}$ ) by the LMTO-ASA method. We will discuss the effect of the X atom on the local magnetic moments on the basis of the obtained electronic structures.

### 2. Crystal structure and method of calculation

The crystal structure of  $\text{Fe}_{16}\text{N}_2$  is of the BCT type shown in figure 1, where there are three types of iron: Fe(4e) on 4e sites, Fe(4d) on 4d sites and Fe(8h) on 8h sites (Jack 1951). The iron atom nearest N is Fe(4e) which has one N nearest neighbour and four Fe(8h) second-nearest neighbours. The Fe atom farthest from N is Fe(4d) which has eight

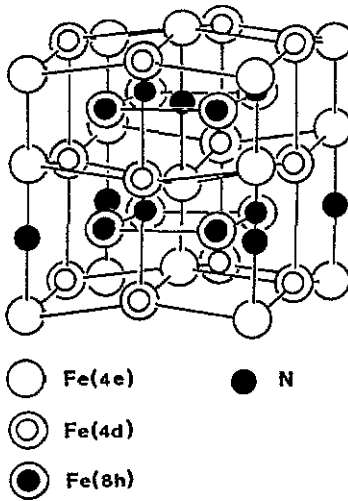


Figure 1. The crystal structure of  $\text{Fe}_{16}\text{X}_2$  ( $\text{X} = \text{B}, \text{C}$  and  $\text{N}$ ).

Table 1. The atomic sphere radii and magnetic moments for  $\text{Fe}_{16}\text{X}_0$  and  $\text{Fe}_{16}\text{X}_2$  ( $\text{X} = \text{B}, \text{C}$  and  $\text{N}$ ). Lattice constant  $a = 5.72 \text{ \AA}$ ,  $c = 6.29 \text{ \AA}$ .

	Radii ( $\text{\AA}$ )		Magnetic moment ( $\mu_B$ )			
	$\text{Fe}_{16}\text{X}_2$	$\text{Fe}_{16}\text{X}_0$	$\text{Fe}_{16}\text{B}_2$	$\text{Fe}_{16}\text{C}_2$	$\text{Fe}_{16}\text{N}_2$	$\text{Fe}_{16}\text{X}_0$
Fe(4e)	1.4005	1.4535	1.95	1.93	1.96	2.37
Fe(4d)	1.4455	1.4535	2.84	2.89	2.91	2.61
Fe(8h)	1.4227	1.4535	2.23	2.28	2.41	2.54
per unit cell			36.73	37.33	38.30	40.20
per Fe			2.30	2.33	2.42	2.51

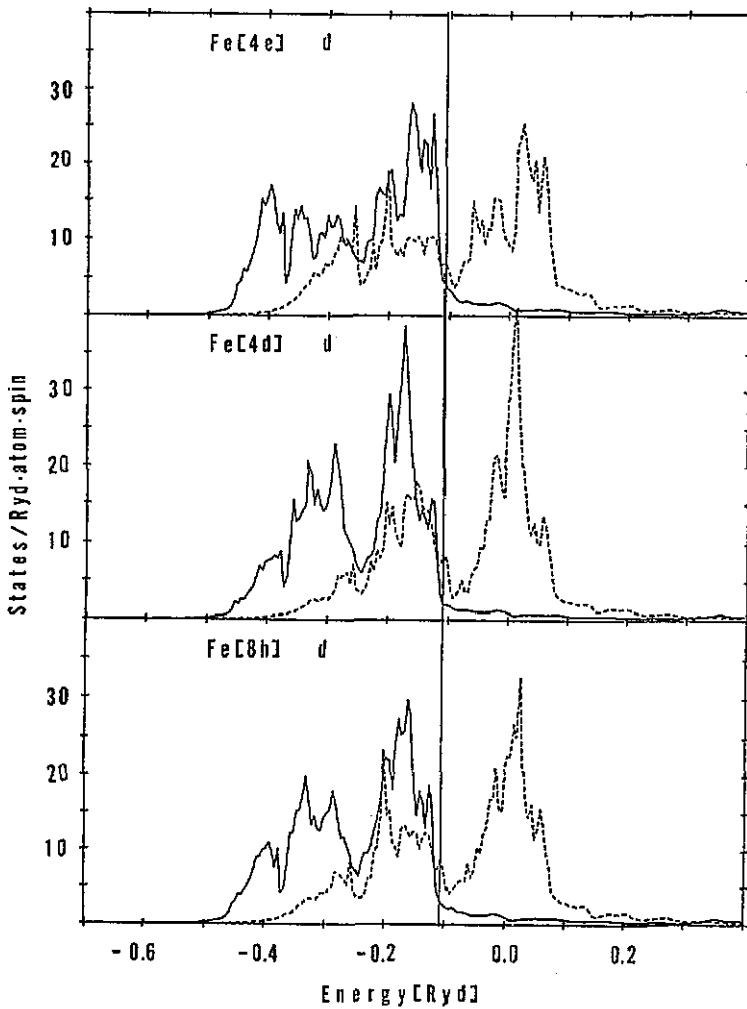
Fe(8h) nearest neighbours and four Fe(4e) second-nearest neighbours. Besides  $\text{Fe}_{16}\text{X}_2$  ( $\text{X} = \text{B}, \text{C}$  and  $\text{N}$ ), we consider the hypothetical lattice of  $\text{Fe}_{16}\text{X}_0$  to investigate the effect of X atoms. The lattice constants of  $\text{Fe}_{16}\text{X}_0$ ,  $\text{Fe}_{16}\text{B}_2$  and  $\text{Fe}_{16}\text{C}_2$  are assumed to be equal to that of  $\text{Fe}_{16}\text{N}_2$ .

The energy eigenvalues were determined by the LMTO-ASA method (Anderson *et al* 1985) and the exchange-correlation potential is within the framework of the LSD approximation (Janak *et al* 1975). The radii  $R_a$  of the atomic spheres were determined so as to preserve the charge neutrality for each atom. The values of  $R_a$  are listed in table 1. The maximum angular momenta to describe the valence states were chosen to be  $l_{\text{max}} = 2$  for all of the constituent atoms. The self-consistency was achieved at 75  $k$ -points in the irreducible Brillouin zone. From the results of 75  $k$ -points, the density of states was determined by the tetrahedral integration method (Rath and Freeman 1975).

### 3. Results and discussion

#### 3.1. Density of states, magnetic moment and hyperfine field

In order to understand the effect of different X atoms on the magnetic properties of  $\text{Fe}_{16}\text{X}_2$ , we compare the densities of states (DOS) for the cases of  $\text{X} = \text{B}, \text{C}, \text{N}$  and



**Figure 2.** The DOS curves of d states of Fe(4e), Fe(4d) and Fe(8h) in  $Fe_{16}X_0$ . The full and broken curves show the DOS of up-spin and down-spin states, respectively. The Fermi level is shown by a vertical line.

$Fe_{16}X_0$ . We see firstly the results of the hypothetical  $Fe_{16}X_0$ . The local DOS are shown in figure 2. The DOS curves of up (majority) spins and down (minority) spins are indicated by the full and broken lines, respectively and the Fermi level by vertical curves. We can see the large valley in the middle of the d bands for both spin states of three types of iron. The peaks in the DOS become sharper for Fe(4e), Fe(8h) and Fe(4d) in that order. The up-spin states are almost occupied and the unoccupied peaks of down-spin states become large for Fe(4e), Fe(8h) and Fe(4d) in that order. This indicates that the magnetic moment increases in this order. This indication is confirmed from the calculated values of the magnetic moments for three types of iron, which are listed in table 1.

Next we consider the results of  $Fe_{16}N_2$  in order to discuss the effect of N. The local DOS are shown in figure 3. The main peaks of the N p states are located below  $-0.4$  Ryd. Those of the N s states located around  $-1.13$  Ryd are not shown. The small peaks for

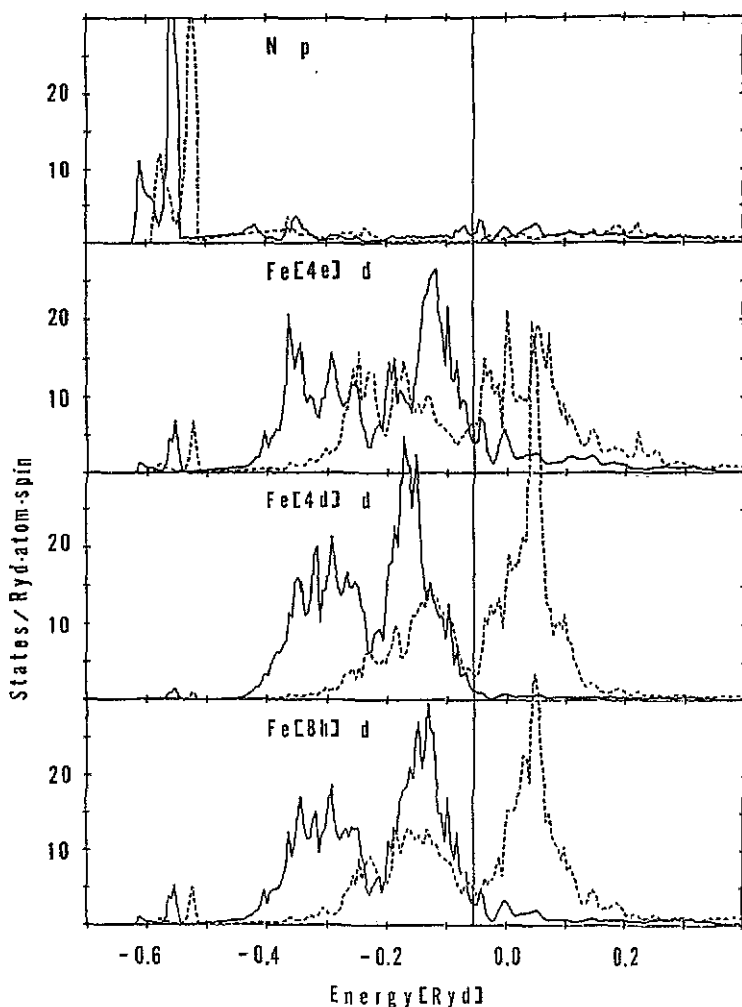
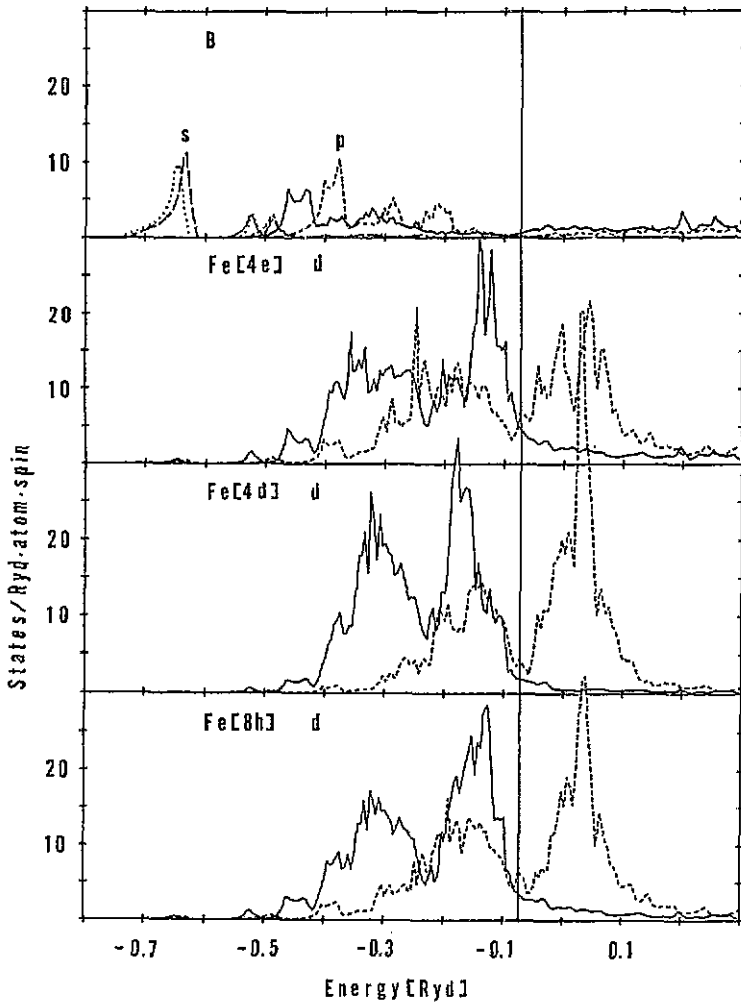


Figure 3. The DOS curves of p states of N and d states of Fe(4e), Fe(4d) and Fe(8h) in  $\text{Fe}_{16}\text{N}_2$ . The full and broken curves show the DOS of up-spin and down-spin states, respectively. The Fermi level is shown by a vertical line.

three types of Fe are also seen below  $-0.4$  Ryd, but are not seen for  $\text{Fe}_{16}\text{X}_0$ . Thus, the hybridization between N valence states and Fe valence states is seen and increases in the order Fe(4e), Fe(8h) and Fe(4d) because the changes in the local DOS decrease in the same order owing to introducing X atoms. Comparing this with the DOS of  $\text{Fe}_{16}\text{X}_0$ , it is found that the d bands are considerably widened for Fe(4e), while the DOS for Fe(8h) and Fe(4d) are hardly distorted, and that the d band tails of up-spin states become larger for Fe(4e) and Fe(8h) owing to introducing N at 2a sites, while the tail becomes smaller for Fe(4d). Thus we can expect that the changes of d-band tails due to introducing N result in the change of magnetic moments of Fe. Comparing the moments for  $\text{Fe}_{16}\text{X}_0$  and  $\text{Fe}_{16}\text{N}_2$  listed in table 1, we found that the moments on Fe(4e) and Fe(8h) decrease, while the moment on Fe(4d) increases in  $\text{Fe}_{16}\text{N}_2$ . It is remarkable that Fe(4d) carries the



**Figure 4.** The DOS curves of s and p states of N and d states of Fe(4e), Fe(4d) and Fe(8h) in  $Fe_{16}B_2$ . The full and broken curves show the DOS of up-spin and down-spin states, respectively. The Fermi level is shown by a vertical line.

large moment of  $2.9\mu_B$ . However, the calculated value of the average moment per Fe is not as large as the experimental value.

In order to investigate whether or not the above features are peculiar to  $Fe_{16}N_2$ , we calculated the electronic structures of  $Fe_{16}B_2$  and  $Fe_{16}C_2$ . The local DOS of  $Fe_{16}B_2$  and  $Fe_{16}C_2$  are shown in figures 4 and 5. Comparing the DOS of  $Fe_{16}X_2$ , it is found that the main peaks of s and p states of X atoms shift to a lower energy region with an increasing number of valence electrons of the X atom. This is because the potential around an X atom becomes deeper for  $X = B, C$  and  $N$  in that order. The DOS shapes of Fe(4e), Fe(4d) and Fe(8h) are very similar for  $X = B, C$  or  $N$ , regardless. Therefore, the effect of an X atom is similar for  $Fe_{16}B_2$ ,  $Fe_{16}C_2$  and  $Fe_{16}N_2$ . However, the minor difference in the DOS shapes results in the difference in the magnetic moments. As seen in table 1, the

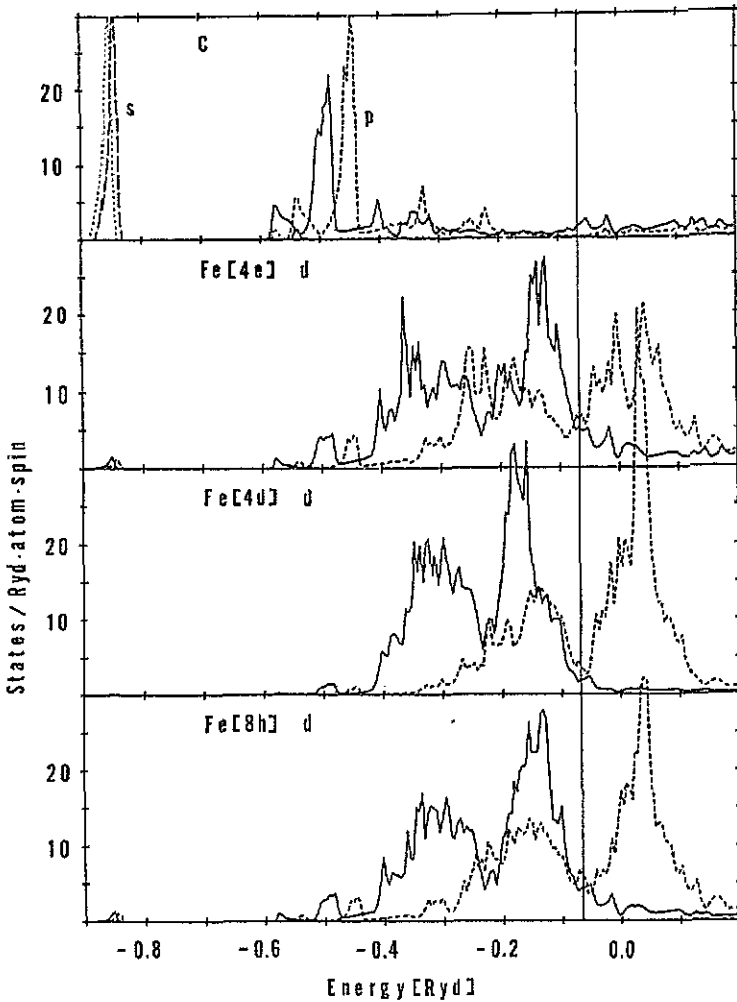


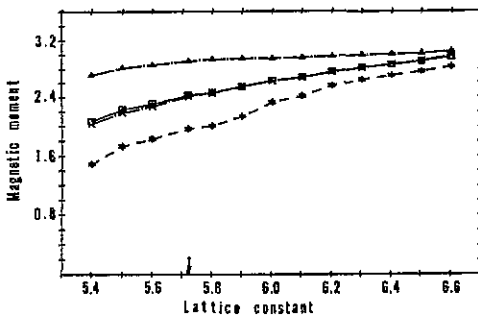
Figure 5. The DOS curves of s and p states of N and d states of Fe(4e), Fe(4d) and Fe(8h) in  $\text{Fe}_{16}\text{C}_2$ . The full and broken curves show the DOS of up-spin and down-spin states, respectively. The Fermi level is shown by a vertical line.

moment per formula unit increases for  $\text{Fe}_{16}\text{B}_2$ ,  $\text{Fe}_{16}\text{C}_2$  and  $\text{Fe}_{16}\text{N}_2$  in that order. It is found that this results mainly from the increment of the local moments on Fe(8h) and Fe(4d).

We calculated the magnetic hyperfine fields for  $\text{Fe}_{16}\text{X}_2$  which are listed in table 2. We considered the contribution through the Fermi contact interaction only. In order to discuss the hyperfine fields in detail we calculated the contributions from inner-core s electrons (denoted by  $H_{\text{core}}$ ) and valence-s electrons (denoted by  $H_{\text{val}}$ ) separately. The signs of these contributions are considered as follows (Ishida *et al* 1991). Since the contribution to  $H_{\text{core}}$  from neighbouring magnetic moments is expected to be small due to the shielding effect, the contribution to  $H_{\text{core}}$  from its own moment is dominant and the sign of  $H_{\text{core}}$  is negative (antiparallel to the self-magnetic moment). On the other hand, the contribution to  $H_{\text{val}}$  from the self-moment is positive but the neighbouring parallel moments contribute negatively to  $H_{\text{val}}$ . In the following discussion, we define

**Table 2.** The hyperfine field at Fe(4e), Fe(4d) and Fe(8h) in  $Fe_{16}X_2$  ( $X = B, C$  and  $N$ ). Values are given in kOe. The hyperfine field  $H$  is separated into two parts:  $H_{\text{core}}$  and  $H_{\text{val}}$ .

	$Fe_{16}B_2$			$Fe_{16}C_2$			$Fe_{16}N_2$		
	$H_{\text{core}}$	$H_{\text{val}}$	$H$	$H_{\text{core}}$	$H_{\text{val}}$	$H$	$H_{\text{core}}$	$H_{\text{val}}$	$H$
Fe(4e)	-205	-32	-237	-201	-30	-231	-197	-44	-241
Fe(4d)	-300	-19	-319	-304	-27	-331	-303	-34	-337
Fe(8h)	-232	-37	-269	-240	-12	-252	-247	-4	-251

**Figure 6.** The lattice parameter dependence of the magnetic moments of Fe(4e) (stars), Fe(4d) (triangles) and Fe(8h) (squares) in  $Fe_{16}N_2$  and the average moment per Fe (crosses).

the positive direction to be parallel to the self-magnetic moment. As seen in table 2, the values of  $H_{\text{core}}$  at Fe(4e), Fe(8h) and Fe(4d) in  $Fe_{16}X_2$  are roughly proportional to the self-magnetic moments in magnitude (about  $-100$  kOe per  $1\mu_B$ ). On the other hand, the values of  $H_{\text{val}}$  are negative because the negative contribution from neighbouring moments is more dominant than the positive contribution from the self-moment. For the case of  $Fe_{16}N_2$ , these opposite contributions almost totally cancel each other at Fe(8h) sites and  $H_{\text{val}}$  at Fe(8h) is one-tenth smaller than the  $H_{\text{val}}$  of Fe(4e). Therefore, the difference between hyperfine fields of Fe(4e) and Fe(8h) is small, though the difference between their magnetic moments is large. Two types of hyperfine fields were observed for three types of Fe in  $Fe_{16}N_2$  (Mitsuoka *et al* 1991). This seems to correspond to our result that the hyperfine fields at Fe(4e) and Fe(8h) sites are nearly equal.  $H_{\text{val}}$  at Fe(8h) increases in magnitude with a decreasing number of X-atom valence electrons, and the difference of hyperfine fields of Fe(4e) and Fe(8h) increases in the order of  $Fe_{16}N_2$ ,  $Fe_{16}C_2$  and  $Fe_{16}B_2$ .

### 3.2. Lattice-constant dependence of the magnetic moment and the hyperfine field

In order to examine whether or not the large magnetic moments appear in the experimental results for  $Fe_{16}N_2$ , we calculated the lattice constant dependence of the magnetic moments and hyperfine fields. Throughout the calculations, the ratio of the atomic sphere radii was fixed to that for  $a = 5.72 \text{ \AA}$ . The magnetic moments on Fe(4e), Fe(4d) and Fe(8h) are shown in figure 6 as functions of the lattice constant. The experimental value of the lattice constant is indicated by an arrow. The moments on Fe(4e), Fe(4d)



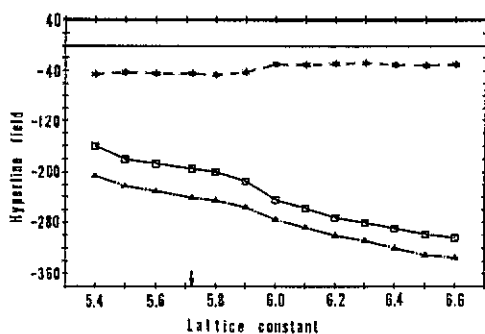


Figure 7. The lattice parameter dependence of the magnetic hyperfine field at Fe(4e) sites in  $\text{Fe}_{16}\text{N}_2$ . The hyperfine field  $H$  (triangles) is separated into two parts:  $H_{\text{core}}$  (squares) and  $H_{\text{val}}$  (stars).

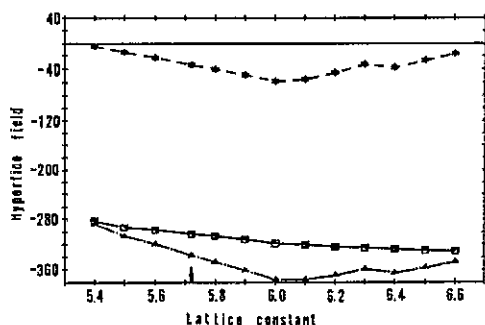


Figure 8. The lattice parameter dependence of the magnetic hyperfine field at Fe(4d) sites in  $\text{Fe}_{16}\text{N}_2$ . The hyperfine field  $H$  (triangles) is separated into two parts:  $H_{\text{core}}$  (squares) and  $H_{\text{val}}$  (stars).

and Fe(8h) increase monotonically with the lattice expansion. The average moment of Fe is nearly equal to that on Fe(8h) and becomes larger than the experimental value of  $2.8\mu_{\text{B}}$  at around  $a = 6.3 \text{ \AA}$ .

The lattice constant dependence of the hyperfine fields on each Fe in  $\text{Fe}_{16}\text{X}_2$  is shown in figures 7, 8 and 9. It is found that the variation of  $H_{\text{core}}$  on each Fe reflects the variation of the self-magnetic moment, that is,  $H_{\text{core}}$  is roughly proportional to the self-moment.  $H_{\text{val}}$  is influenced not only by the self-moment but also by the surrounding moments as described above. Since the change of the moment on Fe(4d) is small, the increment of the moments on the eight first-neighbour Fe(8h) increases the negative contribution to  $H_{\text{val}}$  but the lattice expansion decreases the negative contribution. We can see in figure 8 the former effect below  $a = 6.0 \text{ \AA}$  and the latter effect above  $a = 6.0 \text{ \AA}$  for  $H_{\text{val}}$  at Fe(4d) in  $\text{Fe}_{16}\text{N}_2$ . Thus, the hyperfine field at Fe(4d) has a maximum value in magnitude around  $a = 6.0 \text{ \AA}$ . A similar feature is seen in  $H_{\text{val}}$  at Fe(8h) in figure 9. However, the increment of the positive contribution from the self-moment cancels the increment of the negative contribution from neighbouring Fe(4e) and Fe(4d) moments below  $a = 5.7 \text{ \AA}$ . On the Fe(4e) sites, the increment of the positive contribution from the self-moment cancels almost totally the increment of the negative contribution from neigh-

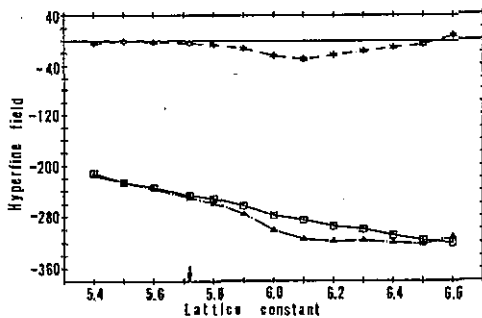


Figure 9. The lattice parameter dependence of the magnetic hyperfine field at Fe(8h) sites in  $\text{Fe}_{16}\text{N}_2$ . The hyperfine field  $H$  (triangles) is separated into two parts:  $H_{\text{core}}$  (squares) and  $H_{\text{val}}$  (stars).

bouring Fe(8h) and Fe(4e) moments over the whole range and the  $H_{\text{val}}$  is nearly constant, as seen in figure 7.

#### 4. Summary

The electronic structures of  $\text{Fe}_{16}\text{X}_2$  ( $X = \text{B}, \text{C}$  and  $\text{N}$ ) were calculated to examine the effect of X atoms on the magnetic properties. The X atoms expand the lattice and the magnetic moment per Fe is enhanced with respect to the moment of pure iron. However, comparing the moments of  $\text{Fe}_{16}\text{X}_0$  and  $\text{Fe}_{16}\text{X}_2$ , the hybridization between valence states of X and d states of Fe suppresses the enhancement of Fe which is near the X atoms. On the Fe(4e) nearest the X atoms, the DOS tails of the d bands become large owing to the hybridization, and the magnetic moments decrease. On the Fe(4d) farthest from the X atoms, the d hole of down-spin states is initially large in the case with no X atoms, and Fe(4d) carries a large magnetic moment. The moment is a little enhanced through the hybridization between d states of Fe(4d) and neighbouring Fe which are influenced by X atoms. Thus, the magnetic moment on Fe(4d) is indirectly enhanced by introducing X atoms. The features described above are seen not only for the case of  $X = \text{N}$  but also for the cases  $X = \text{B}$  and  $\text{C}$ .

We also calculated the hyperfine fields. The hyperfine fields on Fe(4e) and Fe(8h) in  $\text{Fe}_{16}\text{N}_2$  are nearly equal, though their magnetic moments are different. This is explained by considering the difference between the contributions from valence s electrons which depend strongly on the neighbouring magnetic moments. Calculating the lattice constant dependence of the magnetic moment for  $\text{Fe}_{16}\text{N}_2$ , we found that the experimental value of the average Fe moment is obtained at around  $a = 6.3 \text{ \AA}$  which is 10% larger than the experimental value of  $a = 5.72 \text{ \AA}$ .

Mitsuoka *et al* (1984) measured the magnetization of Fe-N compounds and estimated that of  $\text{Fe}_{16}\text{N}_2$  to be  $2.61 \mu_{\text{B}}/\text{Fe}$  which was extrapolated from the values for the low-N concentration. Thus, the magnetization is different for bulk and film samples of  $\text{Fe}_{16}\text{N}_2$ . We should consider the surface and boundary effects for  $\text{Fe}_{16}\text{N}_2$  film grown onto Fe film. Although it is difficult to prepare a bulk sample because  $\text{Fe}_{16}\text{N}_2$  is metastable, we expect that neutron diffraction experiments will be carried out for bulk samples and the magnetic moments of three kinds of Fe in  $\text{Fe}_{16}\text{N}_2$  will be determined. If the value of

the moment for the film is equal to that for the bulk sample, the calculated value is considerably smaller than the experimental one. Thus, we should describe the wavefunctions of d electrons in such a way as to localize d electrons around a nucleus, because the magnetic moment becomes larger for a larger lattice constant. However, we obtained good agreement between the calculated and experimental results with respect to the magnetic moments and the hyperfine fields for  $\text{Fe}_4\text{N}$ , using the same method (Ishida and Kitawatase 1991). The  $\text{Fe}_{16}\text{N}_2$  structure is assumed to be as the  $\text{Fe}_4\text{N}$  structure in which the removal of alternate nitrogen atoms causes distortion (Jack 1951). The magnetic moments of two kinds of iron in  $\text{Fe}_4\text{N}$  are 2.0 and  $3.0\mu_{\text{B}}$  which correspond to the moments of  $\text{Fe}(4e)$  and  $\text{Fe}(4d)$  in  $\text{Fe}_{16}\text{N}_2$ .

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