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Calculation of the magnetic moment of Fe_{16}N_2

Kaoru Miura, Syunji Imanaga and Yoshinori Hayafuji

Sony Corporation Research Centre, 134, Gohdo-cho, Hodogaya-ku, Yokohama 240, Japan

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Abstract. The dependence of the magnetic moment of Fe_{16}N_2 on the distortion of the Fe lattice has been calculated using the discrete variational X_n cluster method. The magnetic moments of Fe_{16}X_2 , where X is B, C, N or a vacancy (vac), have been also calculated. From the calculated results for Fe_{16}X_2 (X = N or vac) and the results for Fe_{16}N_2 calculated with varying distortions of the Fe lattice, we have found that (i) the interaction between the 3d orbital of the first-nearest-neighbour Fe from N (Fe I) extending toward N and the N 2p orbital and (ii) the interaction between the 3d orbital of the second-nearest-neighbour Fe (Fe II) extending toward N and the N 2p orbitals are both weak. We have also found that the presence of N reduces the moments of Fe I and Fe II. The average calculated magnetic moment of Fe_{16}N_2 is $2.25\mu_B$, which is far smaller than the experimental values obtained by Komuro and co-workers, but is in good agreement with experimental results obtained more recently by Takahashi and co-workers.

1. Introduction

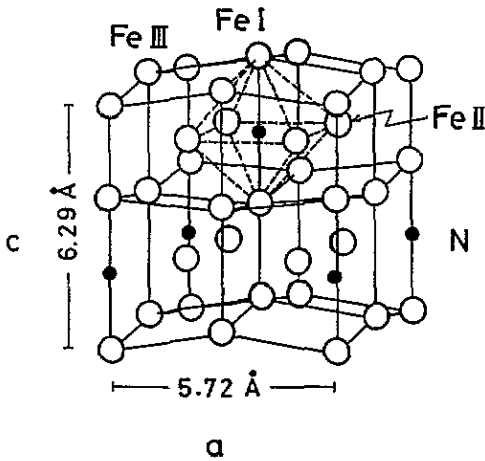
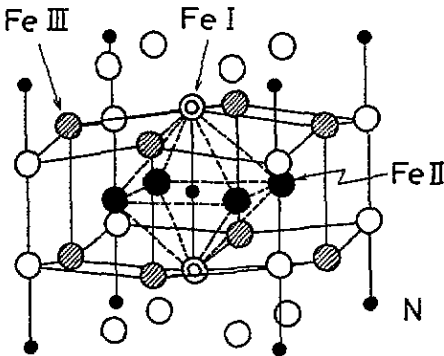
The observation by Kim and Takahashi [1] of the giant magnetic moment of Fe_{16}N_2 in Fe–N films has excited much interest. Many researchers attempted to observe this magnetic moment, but were unable to make single-crystal Fe_{16}N_2 films because of the instability of Fe_{16}N_2 .

Though no one could make single-crystal Fe_{16}N_2 films, the structure of Fe_{16}N_2 had already been determined by Jack [2]. The structure is called a body centred tetragonal (BCT) structure. It is derived from a body centred cubic (BCC) structure, with a distortion of the lattice by N atoms in interstitial sites. Figure 1 shows the BCT structure of Fe_{16}N_2 . As can be seen, this structure contains three Fe sites: Fe I, Fe II and Fe III.

In 1990, Komuro and co-workers [3] succeeded in growing single-crystal Fe_{16}N_2 films by molecular beam epitaxy (MBE). They reported that the average magnetic moment is $3.1\text{--}3.3\mu_B$ at room temperature, a little larger than the $2.8\mu_B$ observed by Kim and Takahashi [1].

After single-crystal Fe_{16}N_2 films were grown successfully, the following calculations [4–10] were reported. Sakuma [4] calculated the magnetic moment of Fe_{16}N_2 using the linear muffin-tin orbital (LMTO) method in the atomic-spheres approximation (ASA). He reported that the average magnetic moment is $2.40\mu_B$, much smaller than the experimental moment of $3.1\text{--}3.3\mu_B$, and that the farthest Fe site from an N atom has the largest magnetic moment ($2.83\mu_B$), while the other two sites have moments of $2.27\mu_B$ and $2.25\mu_B$. The calculated average moment is not in agreement with the experimental moment, whereas the calculated magnetic moments of both Fe_3N and Fe_4N are in good agreement with the experimental moments [4]. Ishida and co-workers [5] also calculated the magnetic moment of Fe_{16}N_2 using the LMTO–ASA method and reported the average magnetic moment to be $2.42\mu_B$.

Although the reason why these calculated results are in disagreement with the experimental results is not known, the following researchers attempted to observe the origin

Figure 1. Crystal structure of Fe_{16}N_2 .Figure 2. Cluster model of Fe_{16}X_2 , where X is B, C, N and VAC, and of Fe_{16}N_2 with varying distortions of the Fe lattice. We regard the three Fe sites nearest the central N atom to be Fe I, Fe II and Fe III.

of the giant magnetic moment. Ishida and co-workers [5] calculated the dependence of the magnetic moment on the lattice constant. From their results, the extrapolated average moment is about $3.1\mu_B$ when the lattice constant is increased by about 17%. But considering the experimental conditions in which single-crystal Fe_{16}N_2 films were grown on InGaAs substrates, which have the same lattice constant as Fe_{16}N_2 [3], there is no possibility that the lattice constant of Fe_{16}N_2 can increase by 17%. Ishida and co-workers [5] and Sakuma and co-workers [9] calculated the magnetic moment of Fe_{16}X_2 where X is B, C, N, O or a vacancy (VAC) and reported that the graph of average moment against X shows a maximum at $X = \text{VAC}$ and that the average moment, even for $X = \text{VAC}$, is about $2.5\mu_B$, which is also smaller than the experimental moment of Fe_{16}N_2 . Even if we take account of the possibility of a lack of N atoms in Fe_{16}N_2 , the calculated result cannot explain the experimental result.

In addition to the above calculations, calculations with varying distortions of the Fe lattice are necessary to clarify the origin of the giant magnetic moment, but only one paper comparing the moment of Fe_{16}N_2 with that of α' -martensite has been published [10]. We have calculated the dependence of the magnetic moments on the distortion of the Fe lattice.

In the present paper, in order to compare the calculated result with the experimental ones and clarify the origin of the giant magnetic moment, we have calculated the magnetic moment of Fe_{16}X_2 , where X = B, C, N and VAC, and the magnetic moment of Fe_{16}N_2 while varying distortions of the Fe lattice, using the discrete variational (DV) X_α cluster

method. The DV X_α method, proposed by Adachi and co-workers [11], is a molecular orbital calculating method.

2. Computational method

The DV X_α method [8] is based on the density functional method using the Slater X_α potential:

$$V_{xc}^\sigma(r) = -3\alpha \left(\frac{3}{4\pi} \rho_\sigma(r) \right)^{1/3} \quad (1)$$

where $\rho_\sigma(r)$ is the charge density at r , σ is the spin index (up or down) and α is a parameter fixed at 0.7. For each spin up or down, we calculate the electronic structure using a one-electron Hamiltonian with (1) as the exchange correlation term.

3. Cluster model

We have calculated the magnetic moment of $Fe_{16}X_2$, where $X = B, C, N$ or VAC, and calculated the magnetic moment of $Fe_{16}N_2$ with varying distortions of the Fe lattice. In the calculation with varying distortions of the Fe lattice, we have changed the structure from α' -martensite to BCT, i.e. the distance between Fe I and N is changed but the distance between Fe II and N is fixed when the structure is changed from α' -martensite to BCC. In order to calculate the magnetic moment using the DV X_α cluster method, we have used the cluster model shown in figure 2. The three Fe sites nearest to the central N atom are referred to as Fe I, Fe II and Fe III.

4. Results

4.1. Magnetic moments of $Fe_{16}X_2$

The magnetic moments of $Fe_{16}X_2$ are shown in table 1. These moments are corrected values: the calculated moments are multiplied by 2.21/2.51 because the moment of the Fe bulk calculated using the present cluster model is $2.51\mu_B$, which is a little larger than the experimental value of Fe bulk of $2.21\mu_B$. The average moment is defined as the sum of the moments with the weight of Fe I : Fe II : Fe III = 1 : 2 : 1 divided by 4, in accordance with the number of equivalent sites in a unit cell. Though the result that the average magnetic moment shows a maximum at $X = VAC$ is in agreement with the calculated results of both Ishida and co-workers [5] and Sakuma and co-workers [9], the average magnetic moments of $Fe_{16}X_2$ with B, C, N and VAC are not in agreement with [5] and [9]. Ishida and co-workers and Sakuma and co-workers reported that the average magnetic moment of $Fe_{16}X_2$ with B, C, N increases monotonically, while the average magnetic moments we have calculated are almost the same. The magnetic moment of each site is not in agreement with [5]: there is a systematic difference between our result and the result in [5], which is consistently lower for the Fe II site for all X. These results may be an artifact of our cluster calculation.

Table 1. The magnetic moment in each site of Fe_{16}X_2 where X is B, C, N and VAC. The values for Fe I, Fe II and Fe III correspond to those in figure 2, and 'average' means the average moment defined as the sum of the moments with the weight of Fe I : Fe II : Fe III = 1 : 2 : 1 divided by 4, in accordance with the number of equivalent sites in unit cell. The unit of each value is μ_B .

Site	VAC	B	C	N
Fe I	2.38	2.10	1.87	1.98
Fe II	2.23	2.07	2.02	2.09
Fe III	2.75	2.78	2.82	2.82
Average	2.40	2.25	2.20	2.25

Table 2. The magnetic moment in each site of Fe_{16}N_2 with the position of Fe I changed. The structure of α' -martensite is defined as 0%, while the structure of BCT, i.e. Fe_{16}N_2 , is defined as 100%. Between the two structures, we have designated three intermediate positions as 25%, 50% and 75%. The unit of each value is μ_B .

Site	0%	25%	50%	75%	100%
Fe I	1.71	1.85	1.90	1.95	1.98
Fe II	2.26	2.24	2.16	2.13	2.09
Fe III	2.87	2.83	2.85	2.82	2.82
Average	2.27	2.30	2.27	2.26	2.25

4.2. Magnetic moment of Fe_{16}N_2 with varying distortions of the Fe lattice

The magnetic moments of Fe_{16}N_2 , with the position of Fe I varied, are shown in table 2. These moments are also corrected moments, the same as shown in table 1. We have defined the structure of α' -martensite to be 0% and the structure of BCT to be 100%, with three intermediate positions corresponding to 25%, 50% and 75%. The average magnetic moment shows a maximum at 25%.

5. Discussion

5.1. Effect of N atom on Fe I and Fe II atoms

The average magnetic moment is almost independent of the position of Fe I as shown in table 2. The average moments of Fe_{16}X_2 where X is B, C or N are almost the same, but the average moment of Fe_{16}X_2 where X is VAC is different, as shown in table 1. From these results, we can conclude that the most important defining characteristic of Fe_{16}X_2 is whether or not X is a vacancy, rather than the degree of distortion of the Fe lattice or the type of X atom. We will consider the effect of the existence of X atoms in the case X = N.

In order to understand the effect of the existence of X atoms, we have compared the density of states in each Fe site for X = N with that for X = VAC. Figures 3(a) and 4(a) show the 3d density of states of Fe I for X = N and X = VAC, respectively, and figures 3(b) and 4(b) show the 3d density of states of Fe II for X = N and X = VAC, respectively. The 2p density of states of the central N atom for X = N is shown in figure 3(c). We do not show the 3d density of states of Fe III because the influence of N atoms on Fe III is smaller than that on Fe I and Fe II. The shapes of these densities of state are different from those of Ishida and co-workers [5]. This may be an artifact of our cluster calculation. But we can observe that the 3d density of states has two peaks in each up and down spin as well as those reported by Ishida *et al*. The bigger peak under the Fermi level in the up spin (over

the Fermi level in the down spin) corresponds to the double-degenerate 3d orbital called $d\gamma$ which is generated by $d(2z^2 - x^2 - y^2)$ and $d(x^2 - y^2)$, while the smaller peak at a lower energy level than the bigger peak's energy level corresponds to the triple-degenerate 3d orbital called $d\epsilon$, which is generated by $d(yz)$, $d(zx)$ and $d(xy)$. The $d(2z^2 - x^2 - y^2)$ orbital of Fe I which is one of the $d\gamma$ orbitals makes a bond with the $p(z)$ orbital of N which is one of the N 2p orbitals, while the $d(xy)$ orbital of Fe II which is one of the $d\epsilon$ orbitals makes a bond with the $p(x)$ and $p(y)$ orbitals of the N 2p orbitals. The $d(yz)$ and $d(zx)$ orbitals of Fe I make a bond with those of Fe II. As shown in figures 3(a) to (c), around the energy level of the peak $d\gamma$ of Fe I, the 2p density of states of N is very small. From this fact, it seems that both the interaction between the Fe I 3d orbital and the N 2p orbital is weak. This conclusion is in good agreement with the calculated result of Fe_4N [12]. Comparing the density of states of Fe I in figure 4(a), for $X = VAC$, with that in figure 3(a), for $X = N$, the peak $d\gamma$ for $X = VAC$ is bigger than that for $X = N$. In spite of our cluster calculation, this result is in agreement with the result of Ishida and co-workers [5]. From the fact that the peak $d\gamma$ for $X = VAC$ is bigger than that for $X = N$, considering that the $d(2z^2 - x^2 - y^2)$ orbital of Fe I makes a bond with the $p(z)$ orbital of N, it seems that the interaction between the Fe I 3d orbital and the N 2p orbital is weak.

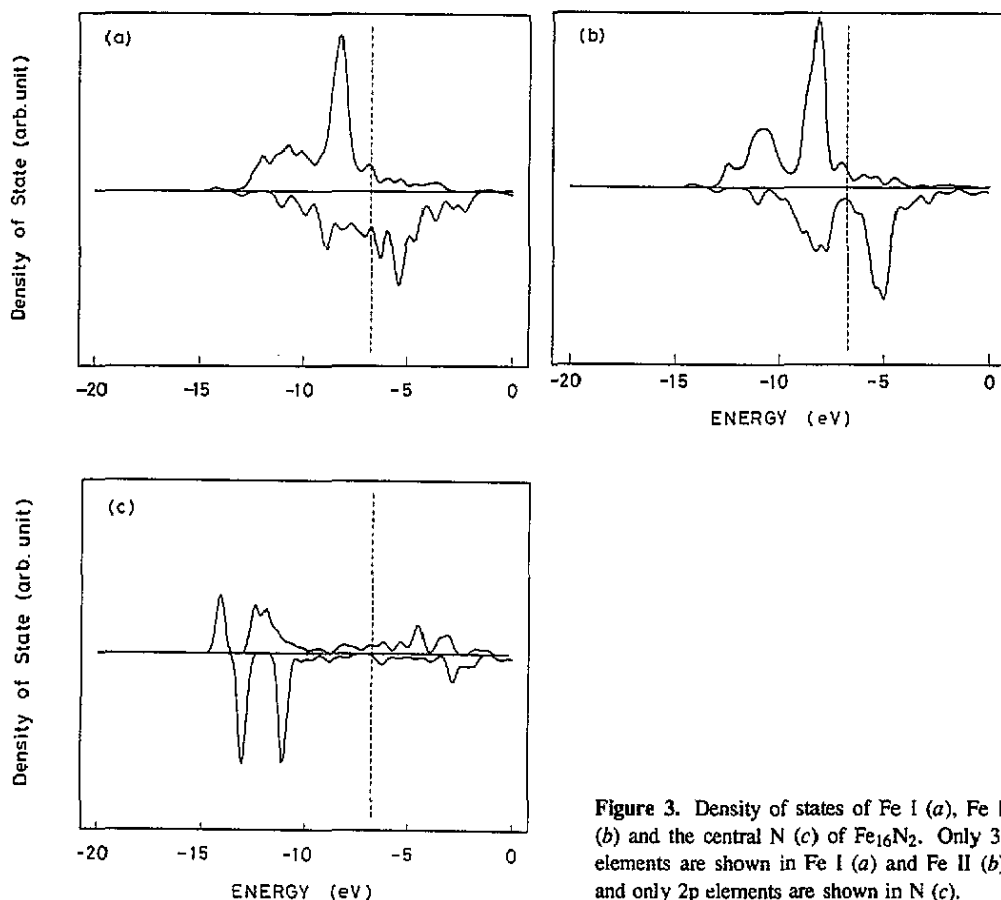


Figure 3. Density of states of Fe I (a), Fe II (b) and the central N (c) of $Fe_{16}N_2$. Only 3d elements are shown in Fe I (a) and Fe II (b), and only 2p elements are shown in N (c).

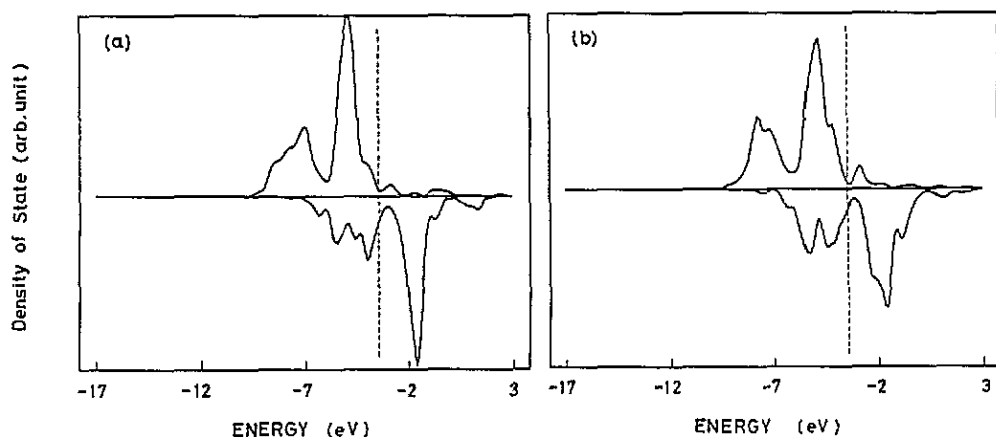


Figure 4. Density of states of Fe I (a) and Fe II (b) of Fe_{16}X_2 where $\text{X} = \text{vac}$. Only 3d elements are shown.

We have compared the dependence of the density of states of both Fe I and Fe II on the position of Fe I. Three results, for 0%, 50% and 100%, are shown in figures 5(a)–(c) for Fe I, and figures 6(a)–(c) for Fe II. For Fe I, as the distance between Fe I and N increases, the peak $d\gamma$ seems to be bigger, while the peak $d\epsilon$ seems to be smaller, as is shown in figure 5. For Fe II, as the distance between Fe I and N increases, the peak $d\gamma$ seems to be bigger, while the peak $d\epsilon$ also seems to be smaller, as is shown in figure 6. For Fe I, considering that the $d(2z^2 - x^2 - y^2)$ orbital of Fe I, which is one of the $d\gamma$ orbitals, makes a bond with the $p(z)$ orbital of N, it seems that the interaction between the Fe I 3d orbital and the N 2p orbital is weak. Moreover, considering that the $d(yz)$ and $d(zx)$ orbitals of Fe I make a bond with those of Fe II, it is natural that the peak $d\epsilon$ becomes smaller because of a smaller overlap between the $d\epsilon$ orbitals of Fe I and those of Fe II as the distance between Fe I and N increases, i.e. the distance between Fe I and Fe II increases. For Fe II, considering that the $d(yz)$ and $d(zx)$ orbitals of Fe II make a bond with those of Fe I, it is natural that the peak $d\epsilon$ becomes smaller because of a smaller overlap between the $d\epsilon$ orbitals of Fe II and those of Fe I. It seems that electrons move from $d\epsilon$ orbitals to $d\gamma$ ones, and thus the $d\gamma$ peak becomes bigger.

5.2. Comparison of the calculated and the experimental result

Because the moments of Fe I and Fe II are smaller than the moment of the Fe bulk as shown in table 1, we can say that the existence of X atoms reduces the moments of Fe atoms around X atoms. In fact, the average calculated moment of Fe_{16}X_2 , as shown in table 1, is about $2.25\mu_B$, which is only a little larger than the moment of the Fe bulk. Moreover, the average moment is largest for $\text{X} = \text{vac}$. This is a general result found in all interstitial magnets [13]. The average calculated moment of Fe_{16}N_2 , and even the moment of Fe_{16}X_2 for $\text{X} = \text{vac}$, is smaller than the experimental result [3] of $3.1\text{--}3.3\mu_B$. Sakuma and co-workers [4, 9] and Ishida and co-workers [5] reported the same results. We cannot explain why the calculated result is not in agreement with the experimental results. Very recently, Takahashi and co-workers [14] reported that the moment of Fe_{16}N_2 , which was synthesized by plasma and sputtering evaporation, is a little larger ($2.23\text{--}2.43\mu_B$) than the moment of the Fe bulk of $2.21\mu_B$. This experimental result is in good agreement with

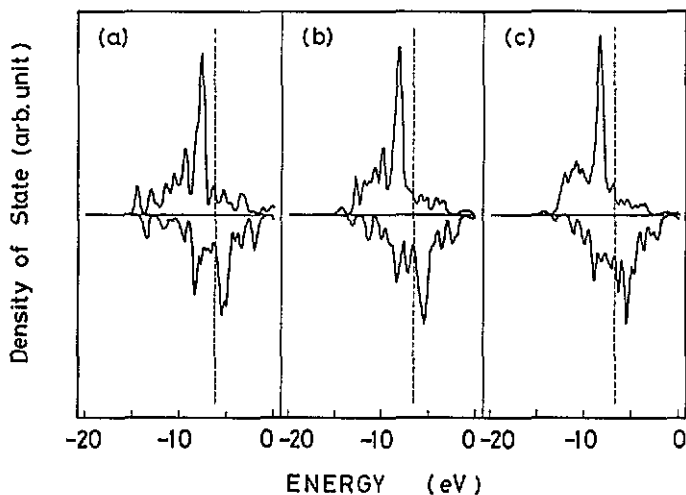


Figure 5. Density of states of Fe I of Fe_{16}N_2 with the position of Fe I varied: 0% (a), 50% (b) and 100% (c).

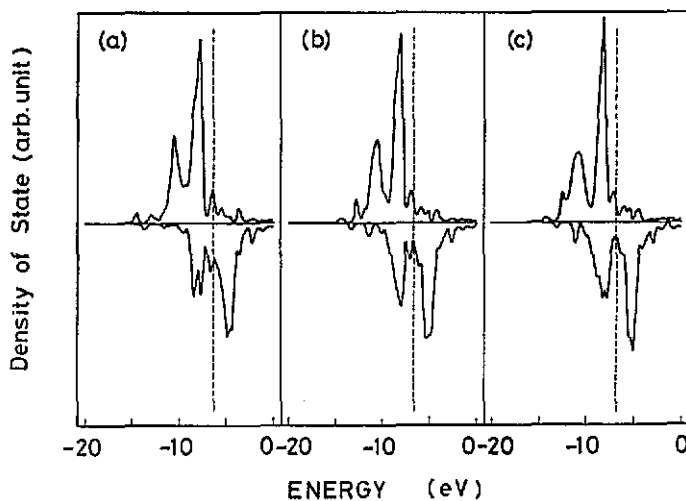


Figure 6. Density of states of Fe II of Fe_{16}N_2 with the position of Fe I varied: 0% (a), 50% (b) and 100% (c).

our calculated result as well as the results of Sakuma and Ishida. We expect that more experimental results will be reported in the near future.

6. Conclusion

The dependence of the magnetic moment of Fe_{16}N_2 on distortions of the Fe lattice has been calculated using the DV X_α cluster method. The magnetic moments of Fe_{16}X_2 , where X is

B, C, N or VAC, have also been calculated. From a comparison of the density of states for $X = N$ with those for $X = \text{VAC}$, and the dependence of the density of states on the distortion of the Fe lattice, we have found that both the interaction between the Fe I 3d orbital and the N 2p orbital and the interaction between the Fe II 3d orbital and the N 2p orbitals are weak, and that the existence of N atoms reduces the moments of Fe I and Fe II. The average calculated magnetic moment of Fe_{16}N_2 is $2.25\mu_B$, which is far smaller than the previous experimental result of $3.1\text{--}3.3\mu_B$. Even the moment of Fe_{16}X_2 for $X = \text{VAC}$ of $2.40\mu_B$ is smaller than the experimental result. But the very recent experimental result of $2.23\text{--}2.43\mu_B$ is in good agreement with our calculated results. We expect that more experimental results will be reported in the near future and we must compare our calculated result with them.

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References

- [1] Kim T K and Takahashi M 1972 *Appl. Phys. Lett.* **20** 492
- [2] Jack K H 1951 *Proc. R. Soc. A* **208** 216
- [3] Komuro M, Kozono Y, Hanazono M and Sugita Y 1990 *J. Appl. Phys.* **67** 5126
- [4] Sakuma A 1991 *J. Magn. Magn. Mater.* **102** 127
- [5] Ishida S, Kitawatase K, Fujii S and Asano S 1992 *J. Phys.: Condens. Matter* **4** 765
- [6] Ishida S and Kitawatase K 1992 *J. Magn. Magn. Mater* **104**–**107** 1933
- [7] Mater S 1992 *Z. Phys.* **B 87** 91
- [8] Sawada H, Nogami A and Mtsumiya T 1993 *Computer Aided Innovation of New Materials* ed M Doyama, J Kimura, M Tanaka and R Yamamoto (New York: Elsevier) p 213
- Min B I 1993 *Int. J. Mod. Phys.* **B 7** 729
- [9] Sakuma A, Sugita Y and Takeda S 1992 *Proc. Int. Conf. on Ferrites '92*
- [10] Zhi-qiang Li 1993 *J. Phys.: Condens. Matter* **5** 1411
- [11] Adachi H, Tsukada M and Satoko C 1978 *J. Phys. Soc. Japan* **45** 875
- [12] Wei Zhou, Li-jia Qu and Qi-ming Zhang 1989 *Phys. Rev.* **B 40** 6393
- [13] Beuerle T and Fahnle M 1992 *Phys. Status Solidi* **b 174** 257
- Fahnle M and Beuerle T 1993 *Phys. Status Solidi* **b 177** K95
- [14] Takahashi M, Shoji H, Takahashi H, Wakiyama T, Kinoshita M and Ohta W 1993 *Proc. INTERMAG '93*