

Electronic structure and magnetism of intermetallic mixed compound $Mn_4N_{1-x}C_x$

Hisashi SHIMIZU*, Kiyosi TERAQ, Kazuko MOTIZUKI** and Naoshi SUZUKI†

Department of Physics, Faculty of Science, Shinshu University,
1-1, Asahi 3, Matsumoto 390, Japan

†Department of Material Physics, Faculty of Engineering Science, Osaka University,
Machikaneyama-cho 1-3, Toyonaka 560, Japan

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Abstract

By applying the recursion method to the intermetallic mixed compound $Mn_4N_{1-x}C_x$ with cubic perovskite-type structure we investigate the effects of substitution of C atoms for N atoms on the electronic structure and the magnetic properties of Mn_4N . By calculating the DOS's for the ferrimagnetic states of both Mn_4N and $Mn_4N_{0.75}C_{0.25}$ we have determined the magnetic moments at two types of Mn site, Mn(I) (corner site) and Mn(II) (face center site), which are antiparallel to each other. The obtained magnetic moment of Mn(I) in $Mn_4N_{0.75}C_{0.25}$ is found to be the same with that in Mn_4N while the absolute value of Mn(II) moment increases by the substitution of C atoms. As the result the total ferromagnetic moment decreases by the substitution of C atoms. These results are in good agreement with the observations.

1 Introduction

Intermetallic manganese compounds, Mn_4N and Mn_4C , have cubic perovskite-type crystal structure (space group O_h^1). Mn atoms occupy the corner and face center sites (these are labelled as Mn(I) and Mn(II), respectively) and N or C atoms occupy the body center sites. Mn_4N becomes a ferrimagnet below $T_N=756$ K and the magnetic moments of Mn(I) and Mn(II) are observed to be different and antiparallel.¹⁻³⁾ The magnitude of the moment of the Mn(I) is four times larger than that of Mn(II). Mn_4C is unstable at room temperature⁴⁾ and it is quite difficult to make a sample of Mn_4C . Therefore little is known about the physical properties of pure Mn_4C . By partially replacing N atoms by C atoms, the magnitude of Mn(II) moment increases whereas the Mn(I) moment changes little, and as the result the total moment

* Present address: Department of Material Physics, Faculty of Engineering Science, Osaka University, Machikaneyama-cho 1-3, Toyonaka 560, Japan

** Present address: Department of Applied Physics, Faculty of Science, Okayama University of Science, Ridai-cho 1-1, Okayama 700, Japan

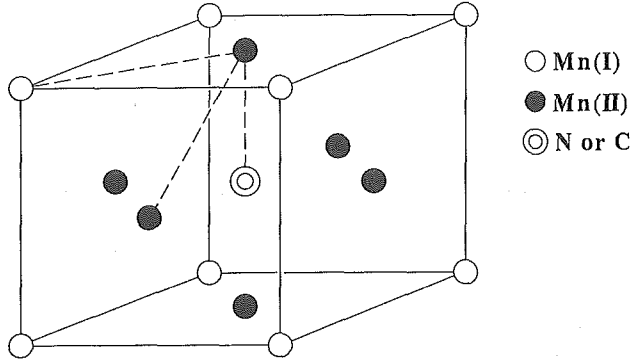


Fig. 1. The crystal structure of Mn_4N and Mn_4C . The transfer integrals are taken into account only for the n.n. atoms connected by the dotted lines.

decreases by the doping.²⁾

The electronic band structures for the non-magnetic state of Mn_4N and Mn_4C and for the ferrimagnetic state of Mn_4N were calculated by Tagawa and Motizuki⁵⁾ by the use of a self-consistent augmented plane wave (APW) method. In the ferrimagnetic state of Mn_4N , the calculated magnetic moments inside the muffin-tin spheres at the Mn(I), Mn(II) and N sites are 3.02, -0.96 and 0.09, respectively, in unit of μ_B /atom. These are compared with 3.85, -0.90 and $0.0\mu_B$ /atom, respectively, observed at $T=77$ K.³⁾ The total moment is obtained to be $0.46\mu_B$ /unit cell which is about half of the observed value $1.14\mu_B$ /unit cell.³⁾ They also estimated the magnetic moment of the mixed compound $Mn_4N_{1-x}C_x$, by adopting the rigid band model for a replacement of N atoms by C atoms, *i.e.* the Fermi level is shifted to lower energies with increasing x . The obtained results are not in agreement with the observed ones.

In order to get a local information such as the local density of states at each atomic site, the recursion method is useful and much simpler compared with the APW method. Furthermore, the recursion method is applicable to such random systems like a mixed compound $Mn_4N_{1-x}C_x$. In this paper we investigate the electronic structure of $Mn_4N_{1-x}C_x$ ($x=0, 0.25, 1$) and their magnetic properties by using the recursion method. The formulation for the recursion method is summarized in Sec.2. The results obtained for the non-magnetic and the ferrimagnetic states are shown in Sec.3.

2 Formulation

The starting Hamiltonian is assumed as

$$\begin{aligned}
 \mathcal{H} = & \sum_{ij} \sum_{mn} \sum_{\sigma} |i, m, \sigma\rangle t_{ij}^{mn} \langle j, n, \sigma| + \sum_{i,m} \sum_{\sigma} |i, m, \sigma\rangle E_{im} \langle i, m, \sigma| \\
 & - \sum_{i,m} \sum_{\sigma} |i, m, \sigma\rangle \sigma \Delta_i \langle i, m, \sigma|,
 \end{aligned} \tag{1}$$

where $|i, m, \sigma\rangle$ denotes the atomic wave function of the m -th orbital with spin σ ($= \pm \frac{1}{2}$) at the i -th atom. The orthogonality relation

$$\langle i, m, \sigma | j, n, \sigma' \rangle = \delta_{ij} \delta_{mn} \delta_{\sigma\sigma'} \quad (2)$$

is assumed. The first term in the Hamiltonian represents the transfer terms between the nearest neighboring (n.n.) Mn(I) and Mn(II), Mn(II) and Mn(II), and Mn(II) and N or C as shown in Fig. 1, and t_{ij}^{mn} describes the transfer integral between the m -th orbital of the i -th atom and the n -th orbital of the j -th atom. In the second term E_{im} denotes the site energy of the m -th orbital at the i -th site. The last term of the Hamiltonian describes the exchange splitting for each atomic state in the ferrimagnetic state. The exchange splitting Δ_i is assumed to be orbital independent. In the non-magnetic state this last term is vanishing.

In the recursion method⁶⁾ we first construct from the basis functions $|i, m, \sigma\rangle$ the new orthonormal basis functions which tri-diagonalize the Hamiltonian (1). The construction of the new basis functions are performed in a recursive way as follows. We first choose an initial atomic state $|i_0, m_0, \sigma\rangle \equiv |0\rangle$ and then a new basis function $|1\rangle$ which is orthogonal to $|0\rangle$ is determined from

$$\mathcal{H}|0\rangle = a_0|0\rangle + b_1|1\rangle. \quad (3)$$

Since the Hamiltonian (1) is diagonal with respect to spin states, we drop the spin suffix σ for simplicity from now on. If we choose a_0 as $a_0 = \{0|\mathcal{H}|0\rangle$, we obtain the orthogonality relation

$$\{0|1\rangle = 0. \quad (4)$$

The value of b_1 can be determined from the normalization condition $\{1|1\rangle = 1$ and given by

$$|b_1|^2 = \{0|(\mathcal{H} - a_0)^\dagger(\mathcal{H} - a_0)|0\rangle. \quad (5)$$

Next, we operate the Hamiltonian to the new basis function $|1\rangle$ and express the result as follows:

$$\mathcal{H}|1\rangle = c_0|0\rangle + a_1|1\rangle + b_2|2\rangle. \quad (6)$$

From eq. (6), the following two relations are obtained:

$$\{0|\mathcal{H}|1\rangle = c_0 + b_2\{0|2\rangle, \quad \{1|\mathcal{H}|1\rangle = a_1 + b_2\{1|2\rangle. \quad (7)$$

Then if c_0 and a_1 are chosen as

$$\{0|\mathcal{H}|1\rangle = c_0, \quad \{1|\mathcal{H}|1\rangle = a_1, \quad (8)$$

the following orthogonality is satisfied:

$$\{0|2\rangle = \{1|2\rangle = 0. \quad (9)$$

Furthermore, c_0 equals b_1 because

$$\{1|\mathcal{H}|0\rangle = a_0\{1|0\rangle + b_1\{1|1\rangle = b_1. \quad (10)$$

The value of b_2 is determined by using the normalization condition $\{2|2\rangle = 1$. After repeating a similar procedure, we get the general relation as follows:

$$\mathcal{H}|\ell\rangle = b_\ell|\ell-1\rangle + a_\ell|\ell\rangle + b_{\ell+1}|\ell+1\rangle, \quad (11)$$

$$a_\ell = \{\ell|\mathcal{H}|\ell\rangle \quad (12)$$

$$|b_{\ell+1}|^2 = |(\mathcal{H} - a_\ell)|\ell\rangle - b_\ell|\ell-1\rangle|^2, \quad (13)$$

$$\{\ell|\ell'\rangle = \delta_{\ell\ell'} \quad (14)$$

with

$$|0\rangle \equiv |i_0, m_0, \sigma\rangle, \quad |-1\rangle \equiv 0.$$

The local density of states (DOS) arising from the m_0 orbital with spin σ at the i_0 site is given by

$$\begin{aligned} D_{m_0, \sigma}^{i_0}(E) &= -\frac{1}{\pi} \text{Im} \langle i_0, m_0, \sigma | \frac{1}{E - \mathcal{H}} | i_0, m_0, \sigma \rangle \\ &= -\frac{1}{\pi} \text{Im} \{0 | \frac{1}{E - \mathcal{H}} | 0\rangle. \end{aligned} \quad (15)$$

Hence $D_{m_0, \sigma}^{i_0}(E)$ can be obtained by calculating the imaginary part of the $(0,0)$ component of the inverse matrix of $E - \mathcal{H}$. Since the matrix representation of the Hamiltonian with respect to the new basis function $|\ell\rangle$ becomes

$$\mathcal{H} = \begin{pmatrix} a_0 & b_1 & 0 & 0 & \cdots \\ b_1 & a_1 & b_2 & 0 & \\ 0 & b_2 & a_2 & b_3 & \ddots \\ 0 & 0 & b_3 & & \ddots \\ \vdots & & \ddots & \ddots & \ddots \end{pmatrix}, \quad (16)$$

$D_{m_0, \sigma}^{i_0}(E)$ can be expressed by

$$D_{m_0, \sigma}^{i_0}(E) = -\frac{1}{\pi} \text{Im} \frac{D_1}{D_0}, \quad (17)$$

where D_0 and D_1 are defined by

$$D_0 = \begin{vmatrix} E - a_0 & -b_1 & 0 & \cdots \\ -b_1 & E - a_1 & -b_2 & \\ 0 & -b_2 & E - a_2 & \ddots \\ \vdots & & \ddots & \ddots \end{vmatrix}, \quad (18)$$

$$D_1 = \begin{vmatrix} E - a_1 & -b_2 & 0 & \cdots \\ -b_2 & E - a_2 & -b_3 & \\ 0 & -b_3 & E - a_3 & \ddots \\ \vdots & & & \ddots \end{vmatrix}. \quad (19)$$

Now we express D_0 as

$$D_0 = (E - a_0)D_1 - b_1^2 D_2, \quad (20)$$

where

$$D_2 = \begin{vmatrix} E - a_2 & -b_3 & 0 & \cdots \\ -b_3 & E - a_3 & -b_4 & \\ 0 & -b_4 & E - a_4 & \ddots \\ \vdots & & & \ddots \end{vmatrix}, \quad (21)$$

and then $D_{m_0, \sigma}^{i_0}(E)$ is written in the following form:

$$D_{m_0, \sigma}^{i_0}(E) = -\frac{1}{\pi} \text{Im} \frac{1}{E - a_0 - b_1^2 \frac{D_2}{D_1}}. \quad (22)$$

Repeating the same procedure for $D_2/D_1, \dots$, we can express $D_{m_0, \sigma}^{i_0}(E)$ by the following continued fraction:

$$D_{m_0, \sigma}^{i_0}(E) = -\frac{1}{\pi} \text{Im} \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \frac{b_3^2}{\ddots}}}}. \quad (23)$$

If the values of a_ℓ and b_ℓ converge to some constant values a and b , respectively, for $\ell \geq L$, then $D_{m_0, \sigma}^{i_0}(E)$ is further rewritten as

$$D_{m_0, \sigma}^{i_0}(E) = -\frac{1}{\pi} \text{Im} \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{\ddots \frac{b^2}{E - a_{L-1} - \Omega(E)}}}}, \quad (24)$$

where

$$\begin{aligned} \Omega(E) &= E - a - \frac{b^2}{E - a - \frac{b^2}{\ddots}} \\ &= E - a - \frac{b^2}{\Omega}. \end{aligned} \quad (25)$$

Solving eq. (25) for Ω we obtain

$$\Omega(E) = \frac{1}{2} [E - a \pm \sqrt{(E - a)^2 - b^2}]. \quad (26)$$

The density of states exists for the energy range in which $\Omega(E)$ is complex, *i.e.* for $|E - a| < |b|$.

In practical calculations for $\text{Mn}_4\text{N}_{1-x}\text{C}_x$, we take into account only the $3d$ orbitals for Mn atom and the $2p$ orbitals for N or C atom. The transfer integral between two atoms can be represented by using the Slater-Koster (SK) two center integrals $t(dd\sigma)$ *etc.* and the direction cosine of the vector connecting the two atoms. As mentioned before and as shown in Fig. 1 we consider the transfer integrals only for the n.n. atoms. Therefore we have three kinds of SK integrals, $t(dd\sigma)$, $t(dd\pi)$ and $t(dd\delta)$, for the n.n. Mn(I) and Mn(II) and for the n.n. Mn(II) and Mn(II), and two kinds of SK integrals, $t(pd\sigma)$ and $t(pd\pi)$, for the n.n. Mn(II) and N (or C). We have further considered different orbital energies for different atoms. For the purpose to evaluate the SK integrals and the orbital energies, we have performed the tight-binding band calculation for the non-magnetic state of Mn_4N and Mn_4C , and determined them so as to reproduce the band energies at the symmetry points in the Brillouin zone calculated by the APW method.⁵⁾ Their determined values are listed in Table 1. The SK integrals for the n.n. Mn(I)-Mn(II) and the n.n. Mn(II)-Mn(II) are different in principle from symmetry although their interatomic distances are the same. For simplicity,

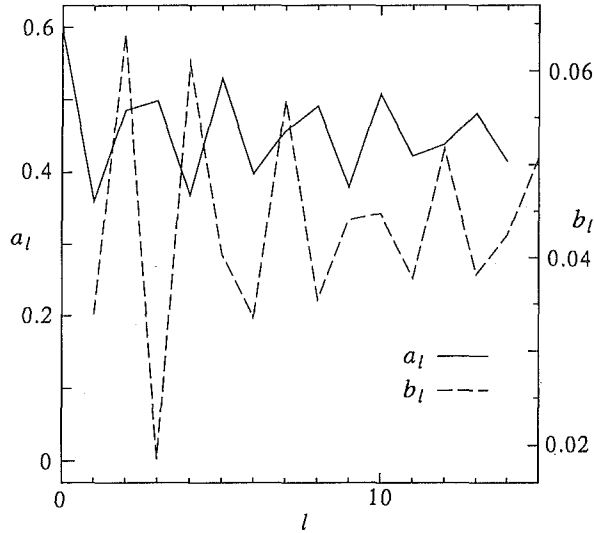


Fig. 2. The recursion coefficients a_l and b_l for the non-magnetic state of Mn_4N in case the initial orbital state is chosen as $3d\gamma(x^2 - y^2)$ of Mn(II).

however, we have assumed the same SK integrals for both the n.n. Mn(I)-Mn(II) and the n.n. Mn(II)-Mn(II). It is seen from Table I that large differences between Mn_4N and Mn_4C lie in the values of the SK integral $t(pd\pi)$ and the orbital energy E_p .

3 Results

(1) Mn_4N and Mn_4C

We first applied the recursion method to the non-magnetic state of Mn_4N and Mn_4C . Figure 2 shows the recursion coefficients a_ℓ and b_ℓ for the non-magnetic state of Mn_4N when the initial state is chosen as $3d\gamma(x^2-y^2)$ of Mn(II). It is seen certainly that a_ℓ and b_ℓ show converging behavior for large ℓ . In actual calculation we have adopted an approximate procedure, *i.e.* we have assumed $a_\ell = a$ and $b_\ell = b$ for $\ell \geq 14$. The values of a and b have been evaluated by taking the average over $\ell=12, 13$ and 14 . Then, the local DOS of Mn(II) $3d\gamma(x^2-y^2)$ orbital is calculated from eq.(24). Carrying out the same calculational procedure for other atomic orbitals we have calculated the partial DOS's of Mn(I) $3d$, Mn(II) $3d$ and N $2p$ (or C $2p$) and the total DOS. The results are shown in Fig. 3(a) for Mn_4N and in Fig. 3(b) for Mn_4C .

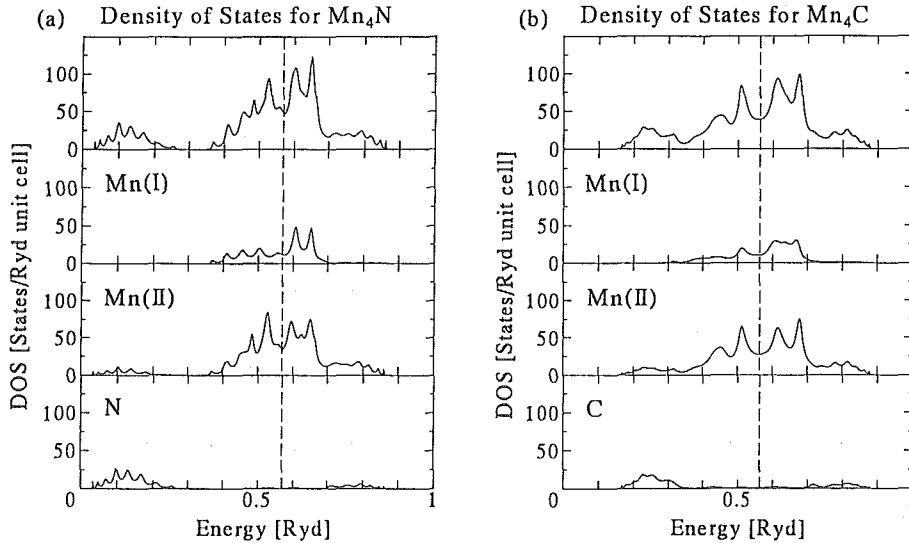


Fig. 3. The total and partial DOS's for the non-magnetic state of (a) Mn_4N and (b) Mn_4C .

The total DOS of Mn_4N is divided into three parts: (i) the low energy part between 0 and 0.3 Ryd, (ii) the intermediate energy range between 0.4 and 0.7 Ryd and (iii) the high energy part between 0.7 and 0.9 Ryd. The $3d$ orbitals of Mn(II) are hybridized with the $2p$ orbitals of N in part (i) and (iii), and are mixed with the $3d$ orbitals of Mn(I) in part (ii). The $3d$ orbitals of Mn(I) mix little with $2p$ orbitals

Table 1. The Slater-Koster(SK) integrals and the site energies for Mn_4N and Mn_4C (in unit of Ryd).

SK integral		Mn_4N	Mn_4C
Mn(I)-Mn(II) Mn(II)-Mn(II)	$t(dd\sigma)$	-0.03	-0.035
	$t(dd\pi)$	0.025	0.033
	$t(dd\delta)$	0.0	0.0
Mn(II)-N Mn(II)-C	$t(pd\sigma)$	0.12	0.118
	$t(pd\pi)$	0.1	0.08

site energy		Mn_4N	Mn_4C
Mn(I)	E_c	0.61	0.61
	E_γ	0.5	0.5
Mn(II)	$E_c(xy)$	0.55	0.55
	$E_c(yz, zx)$	0.58	0.58
	$E_\gamma(x^2 - y^2)$	0.52	0.52
	$E_\gamma(3z^2 - r^2)$	0.6	0.6
N	E_p	0.28	
C	E_p		0.42

Table 2. The magnetic moment m [μ_B], the DOS [states/(Ryd·atom) or states/(Ryd·unit cell)], the exchange energy I [Ryd] and the exchange splitting Δ [Ryd] in the ferrimagnetic state of Mn_4N . The arrows \uparrow and \downarrow denote the up-spin and the down-spin states, respectively.

	m	$N(E_F)$	I	Δ
Mn(I)	3.9	11(\uparrow)	0.063	0.248
		2.8(\downarrow)		
Mn(II)	-0.88	27(\uparrow)	0.048	0.042
		14(\downarrow)		
N	0.07	0.65(\uparrow)		
		0.46(\downarrow)		
total	1.3	140		

of N because we have neglected the direct transfer between Mn(I) and N. The Fermi level E_F is located in the part (ii). The DOS of Mn_4C is similar to Mn_4N except that the part (i) region of Mn_4C moves to the higher energy side compared with Mn_4N .

To calculate the DOS for the ferrimagnetic state of Mn_4N , the exchange splittings Δ_i are introduced for up and down spin states of the $3d$ orbitals at Mn(I) and Mn(II) sites. We have assumed Δ_i is independent of the orbital m and determined its value so as to reproduce the observed Mn moments of pure Mn_4N . The total and partial DOS's calculated for the ferrimagnetic state of Mn_4N are shown in Fig. 4.

The exchange splittings Δ_i , the values of the DOS's at E_F and the magnetic moments m_i (in unit of μ_B) at each atom are listed in Table 2. As seen from the table very small magnetic moment is induced on the N site through the hybridization between the Mn $3d$ and the N $2p$ orbitals. From the values of the exchange splitting Δ_i and the magnetic moment m_i we have evaluated the exchange energy $I_i = \Delta_i / |m_i|$. The results are 0.063 Ryd for Mn(I) and 0.048 Ryd for Mn(II). These values are comparable with that of fcc Mn, 0.059 Ryd.⁷⁾ By using the total DOS at E_F , the coefficient of the electronic specific heat γ of Mn_4N is estimated to be $24 \text{ mJK}^{-2}\text{mol}^{-1}$. On the other hand, the observed value of γ is $42 \pm 2 \text{ mJK}^{-2}\text{mol}^{-1}$.¹⁾ Then, the mass enhancement factor due to electron correlation and/or electron-phonon interaction is evaluated to be $\lambda = 0.75$.

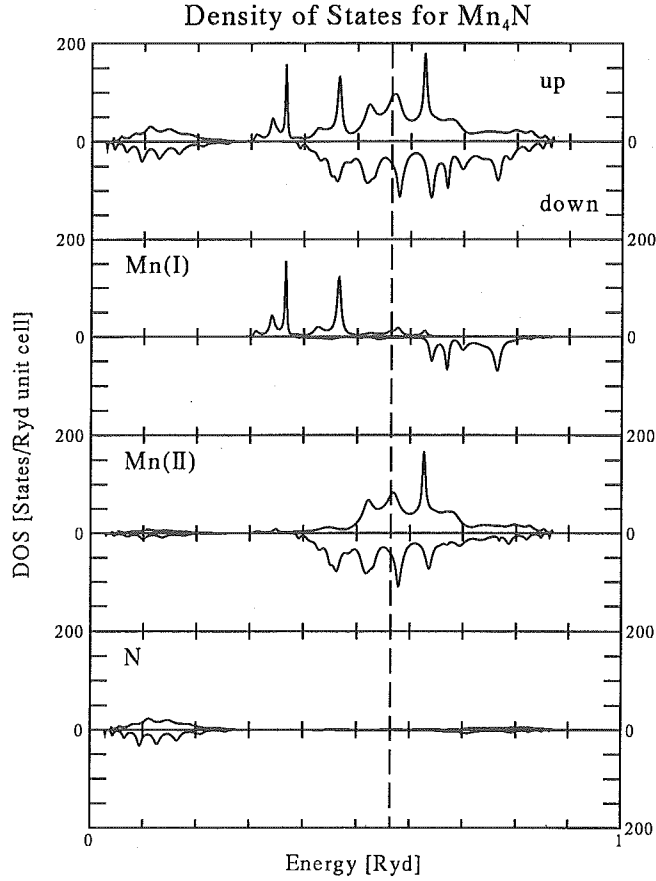


Fig. 4. The total and partial DOS's for the ferrimagnetic state of Mn_4N .

(2) *Mixed compound $Mn_4N_{0.75}C_{0.25}$*

In the calculation of the DOS for the non-magnetic and the ferrimagnetic states of $Mn_4N_{0.75}C_{0.25}$, we have approximated the crystal by a periodic array of clusters each of which consists of eight unit cells ($2 \times 2 \times 2$) of Mn_4N lattice and hence contains 32 Mn atoms, 6 N atoms and 2 C atoms. As shown in Fig. 5 there are three types of clusters, (a), (b) and (c) depending on different C configurations. The ratio of statistical probabilities of (a), (b) and (c) cases is 3 : 3 : 1.

It is further noted that for each type of cluster there exist several inequivalent sites for Mn(I), Mn(II) and N atoms. In calculating the DOS we have taken average over all of the inequivalent atomic sites as well as over all of the C configuration. As for the parameters such as the SK integrals $t(p\delta\sigma)$ etc., the orbital energies of the 3 d or 2 p states and the exchange splitting Δ_i , we have used the values listed in Table

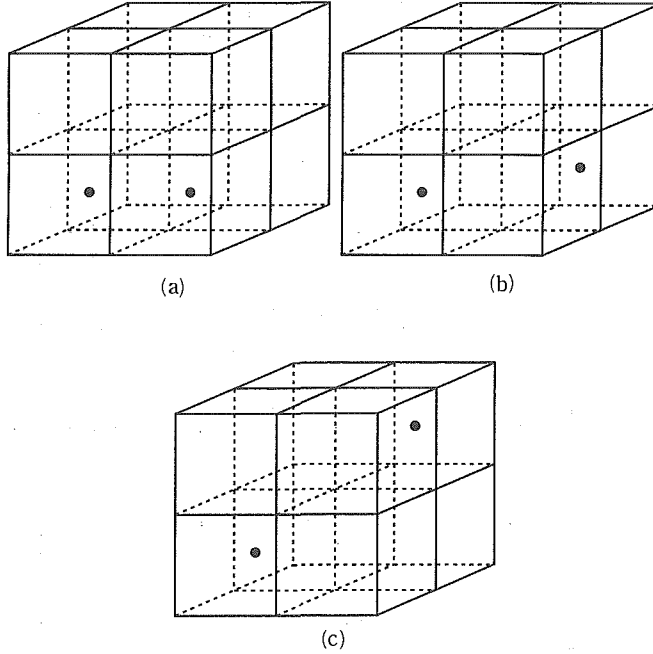


Fig. 5. The three types of C configurations for $2 \times 2 \times 2$ cluster containing 32 Mn atoms, 6 N atoms and 2 C atoms. In the figure only the C positions are depicted.

1 and Table 2. Since C concentration is small, we have used tentatively the same values of $t(dd\sigma)$, $t(dd\pi)$ and $t(dd\delta)$ as those determined for Mn_4N . Furthermore, we have assumed the same exchange splitting as for Mn_4N .

The averaged DOS's calculated by the recursion method for the non-magnetic and ferrimagnetic states of $\text{Mn}_4\text{N}_{0.75}\text{C}_{0.25}$ are shown in Figs. 6 (a) and 6 (b), respectively.

Table 3. The magnetic moment m [μ_B] and the DOS [states/(Ryd \cdot atom) or states/(Ryd \cdot unit cell)] in ferrimagnetic $\text{Mn}_4\text{N}_{0.75}\text{C}_{0.25}$. The arrows \uparrow and \downarrow denote the up-spin and the down-spin states, respectively.

	m	$N(E_F)$
Mn(I)	3.9	12 (\uparrow)
		4.3 (\downarrow)
Mn(II)	-0.95	26 (\uparrow)
		16 (\downarrow)
total	1.1	141

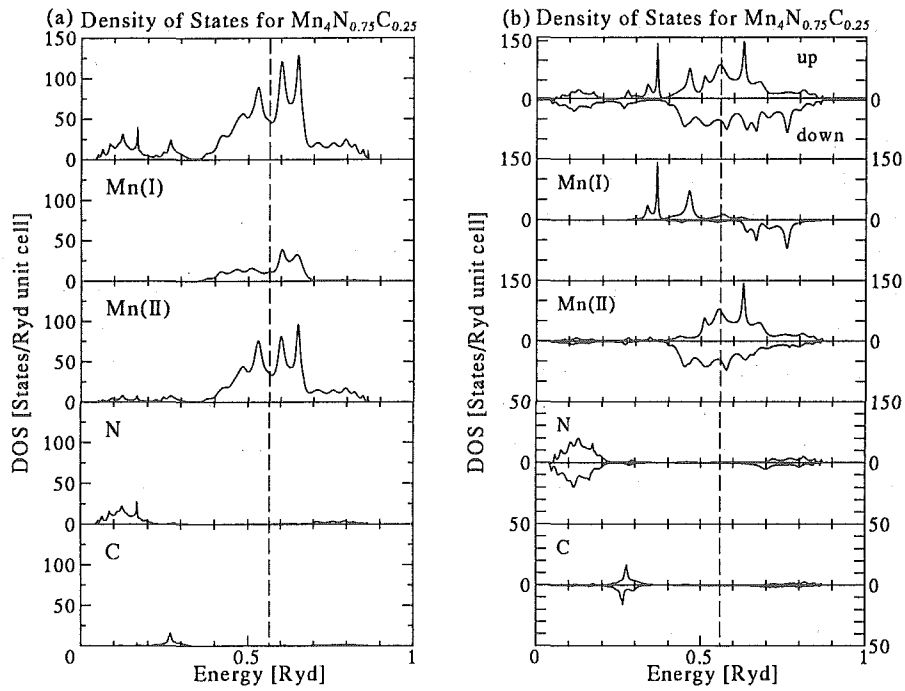


Fig. 6. The total and partial DOS's for the mixed compound $Mn_4N_{0.75}C_{0.25}$: (a) the non-magnetic state and (b) the ferrimagnetic state.

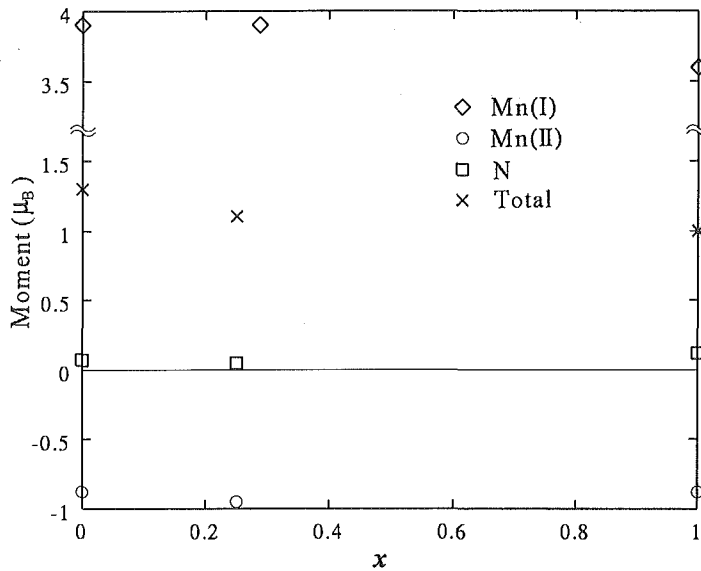


Fig. 7. The total magnetic moment and the magnetic moment at each atomic site calculated for ferrimagnetic $Mn_4N_{1-x}C_x$ ($x = 0, 0.25$ and 1).

The averaged magnetic moment at each atomic site is given in Table 3 together with the DOS's at E_F . In Fig. 7 we show the magnetic moments calculated for ferrimagnetic $Mn_4N_{1-x}C_x$ ($x=0, 0.25$ and 1). Calculations for $x=1$, *i.e.* for pure Mn_4C have been performed by using the same exchange splittings as those of Mn_4N . In the mixed compound $Mn_4N_{0.75}C_{0.25}$, the calculated magnetic moment of Mn(I) is found to be almost unchanged compared with that of Mn_4N while the absolute value of Mn(II) moment increases and in total the net ferromagnetic moment decreases. These results are in good agreement with the observations. The increase of the magnitude of Mn(II) moment by the C substitution may be ascribed to the reduction of the band width of the Mn(II) $3d$ states due to the small SK integrals between Mn(II) and C compared with those between Mn(II) and N. On the other hand, little effect of the C substitution on the Mn(I) moment can be due to our use of the same SK integrals for Mn(I)-Mn(II) as those in pure Mn_4N , which is reasonable assumption for low concentration of C atoms.

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