Electronic structure and magnetism of intermetallic mixed compound $\text{Mn}_4\text{N}_{1-x}\text{C}_x$

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Abstract

By applying the recursion method to the intermetallic mixed compound $\text{Mn}_4\text{N}_{1-x}\text{C}_x$ 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 $\text{Mn}_4\text{N}$. By calculating the DOS's for the ferrimagnetic states of both $\text{Mn}_4\text{N}$ and $\text{Mn}_4\text{N}_{0.75}\text{C}_{0.25}$ 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 $\text{Mn}_4\text{N}_{0.75}\text{C}_{0.25}$ is found to be the same with that in $\text{Mn}_4\text{N}$ 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, $\text{Mn}_4\text{N}$ and $\text{Mn}_4\text{C}$, have cubic perovskite-type crystal structure (space group $O_h^3$). 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. $\text{Mn}_4\text{N}$ 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). $\text{Mn}_4\text{C}$ is unstable at room temperature4) and it is quite difficult to make a sample of $\text{Mn}_4\text{C}$. Therefore little is known about the physical properties of pure $\text{Mn}_4\text{C}$. 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
decreases by the doping.\(^3\)

The electronic band structures for the non-magnetic state of Mn\(_4\)N and Mn\(_4\)C and for the ferrimagnetic state of Mn\(_4\)N were calculated by Tagawa and Motizuki\(^5\) by the use of a self-consistent augmented plane wave (APW) method. In the ferrimagnetic state of Mn\(_4\)N, the calculated magnetic moments inside the muffin-tin spheres at the Mn(1), Mn(II) and N sites are 3.02, −0.96 and 0.09, respectively, in unit of \(\mu_B/\text{atom}\). These are compared with 3.85, −0.90 and 0.005\(\mu_B/\text{atom}\), respectively, observed at \(T=77\text{ K}\).\(^3\) The total moment is obtained to be 0.46\(\mu_B/\text{unit cell}\) which is about half of the observed value 1.14\(\mu_B/\text{unit cell}\).\(^3\) They also estimated the magnetic moment of the mixed compound Mn\(_4\)Ni\(_x\)C\(_{1-x}\), 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\(_4\)Ni\(_{1-x}\)C\(_x\). In this paper we investigate the electronic structure of Mn\(_4\)Ni\(_{1-x}\)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

\[
\mathcal{H} = \sum_{ij} \sum_{nm} \sum_{\sigma} \langle i, m, \sigma | t_{ij}^{nm} | j, n, \sigma \rangle + \sum_{i,m} \sum_{\sigma} \langle i, m, \sigma | E_m | i, m, \sigma \rangle
- \sum_{i,m} \sum_{\sigma} \langle i, m, \sigma | \Delta_i | i, m, \sigma \rangle, \tag{1}
\]

\(t_{ij}^{nm}\): transfer integrals
\(E_m\): single-particle energies
\(\Delta_i\): on-site energy.
Electronic structure and magnetism of intermetallic mixed compound $M_nM_{1-x}C_x$

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

$$<i, m, \sigma | j, n, \sigma'> = \delta_{ii}\delta_{mm}\delta_{\sigma\sigma'}$$

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 $t_{ij}^{m,n}$ 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 $\Delta_i$ is assumed to be orbital independent. In the non-magnetic state this last term is vanishing.

In the recursion method\(^6\) we first construct from the basis functions $|i, m, \sigma>$ 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 $|i_0, m_0, \sigma> = |0>$ and then a new basis function $|1>$ which is orthogonal to $|0>$ is determined from

$$|1> = (\mathcal{H} - a_0|0> + b_1|1>.$$  \hspace{1cm} (3)

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

$$<0|1> = 0.$$ \hspace{1cm} (4)

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

$$|b_1|^2 = <0|(\mathcal{H} - a_0)^+ (\mathcal{H} - a_0)|0>.$$ \hspace{1cm} (5)

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

$$\mathcal{H}|1> = c_0|0> + a_1|1> + b_2|2>.$$ \hspace{1cm} (6)

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

$$<0|\mathcal{H}|1> = c_0 + b_2 <0|2>, \hspace{1cm} <1|\mathcal{H}|1> = a_1 + b_2 <1|2>.$$ \hspace{1cm} (7)

Then if $c_0$ and $a_1$ are chosen as

$$<0|\mathcal{H}|1> = c_0, \hspace{1cm} <1|\mathcal{H}|1> = a_1,$$

the following orthogonality is satisfied:

$$<0|2> = <1|2> = 0.$$ \hspace{1cm} (9)
Furthermore, \( c_0 \) equals \( b_1 \) because
\[
\{1|\mathcal{H}|0\} = a_0\{1|0\} + b_1\{1|1\} = b_1.
\]
The value of \( b_2 \) is determined by using the normalization condition \( \{2|2\} = 1 \). After repeating a similar procedure, we get the general relation as follows:
\[
\mathcal{H}|\ell\rangle = b_1|\ell-1\rangle + a_2|\ell\rangle + b_{t+1}|\ell+1\rangle,
\]
\[
a_t = \{\ell|\mathcal{H}|\ell\}
\]
\[
|b_{t+1}|^2 = |(\mathcal{H} - a_2)|\ell\rangle - b_1|\ell-1\rangle|^2,
\]
\[
\{\ell|\ell'\} = \delta_{\ell\ell'}
\]
with
\[
|0\rangle = |i_0,m_0,\sigma>, ~ |\uparrow\rangle = 0.
\]

The local density of states (DOS) arising from the \( m_0 \) orbital with spin \( \sigma \) at the \( i_0 \) site is given by
\[
D_{i_0,m_0,\sigma}^{\mathcal{H}}(E) = -\frac{1}{\pi}\text{Im}<i_0,m_0,\sigma|\frac{1}{E-\mathcal{H}}|i_0,m_0,\sigma>
\]
\[
= -\frac{1}{\pi}\text{Im} \{0|\frac{1}{E-\mathcal{H}}|0\}. \tag{15}
\]

Hence \( D_{i_0,m_0,\sigma}^{\mathcal{H}}(E) \) 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
\[
\mathcal{H} = \begin{pmatrix}
  a_0 & b_1 & 0 & 0 & \cdots \\
  b_1 & a_1 & b_2 & 0 \\
  0 & b_2 & a_2 & b_3 \\
  0 & 0 & b_3 & \ddots \\
  \vdots & \ddots & \ddots & \ddots
\end{pmatrix}
\]

\( D_{i_0,m_0,\sigma}^{\mathcal{H}}(E) \) can be expressed by
\[
D_{i_0,m_0,\sigma}^{\mathcal{H}}(E) = -\frac{1}{\pi}\text{Im} \frac{D_1}{D_0}, \tag{17}
\]
where \( D_0 \) and \( D_1 \) are defined by
\[
D_0 = \begin{pmatrix}
  E-a_0 & -b_1 & 0 & \cdots \\
  -b_1 & E-a_1 & -b_2 & \\
  0 & -b_2 & E-a_2 & \ddots \\
  \vdots & \ddots & \ddots & \ddots
\end{pmatrix}
\]

\[
D_1 = \begin{pmatrix}
  E-a_0 & -b_1 & 0 & \cdots \\
  -b_1 & E-a_1 & -b_2 & \\
  0 & -b_2 & E-a_2 & \ddots \\
  \vdots & \ddots & \ddots & \ddots
\end{pmatrix}
\]
Now we express $D_0$ as
\[ D_0 = (E - a_0)D_1 - b_1 D_2, \]
where
\[ D_1 = \begin{pmatrix} E - a_1 & -b_2 & 0 & \cdots \\ -b_2 & E - a_2 & -b_3 \\ 0 & -b_3 & E - a_3 & \ddots \\ \vdots & \ddots & \ddots \end{pmatrix}. \]

And then
\[ D_{\pi_n,\sigma}(E) = -\frac{1}{\pi} \text{Im} \frac{1}{E - a_0 - b_1^2 D_0/D_1}. \]

Repeating the same procedure for $D_3/D_4, \ldots$, we can express $D_{\pi_n,\sigma}(E)$ by the following continued fraction:
\[ D_{\pi_n,\sigma}(E) = -\frac{1}{\pi} \text{Im} \frac{1}{E - a_0 - \frac{b_1^2}{b_2} \frac{b_2^2}{b_3} \cdots} \frac{b_1^2}{b_2} \frac{b_2^2}{b_3} \ldots} \frac{b_1^2}{b_2} \frac{b_2^2}{b_3} \cdots} E - a_{l-1} - \frac{b_l^2}{\Omega(E)} \]

If the values of $a_l$ and $b_l$ converge to some constant values $a$ and $b$, respectively, for $\ell \geq L$, then $D_{\pi_n,\sigma}(E)$ is further rewritten as
\[ D_{\pi_n,\sigma}(E) = -\frac{1}{\pi} \text{Im} \frac{1}{E - a_0 - \frac{b_1^2}{b_2} \frac{b_2^2}{b_3} \cdots} \frac{b_1^2}{b_2} \frac{b_2^2}{b_3} \cdots} E - a_{l-1} - \frac{b_l^2}{\Omega(E)} \]

where
\[ \Omega(E) = E - a - \frac{b^2}{E - a - \frac{b^2}{\cdots}} \]
\[ = E - a - \frac{b^2}{\Omega}. \]
Solving eq. (25) for $\Omega$ we obtain

$$\Omega(E) = \frac{1}{2} \left[ E - a \pm \sqrt{(E-a)^2 - b^2} \right].$$  \hspace{1cm} (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 Mn$_4$N$_{1-x}$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 $t(ddd)$ 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$_4$N and Mn$_4$C, and determined them so as to reproduce the band energies at the symmetry points in the Brillouin zone calculated by the APW method.\textsuperscript{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$_4$N in case the initial orbital state is chosen as $3d_{x^2-y^2}$ of Mn(II).](image-url)
however, we have assumed the same SK integrals for both the n.n. \( Mn(II) \)-Mn(II) and the n.n. Mn(II)-Mn(II). It is seen from Table 1 that large differences between \( Mn_4N \) and \( Mn_4C \) lie in the values of the SK integral \( t(pdx) \) 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 \( a_\ell \) and \( b_\ell \) 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 \( a_\ell \) and \( b_\ell \) show converging behavior for large \( \ell \). 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 \( Mn(1) 3d \), \( Mn(II) 3d \) and \( N 2p(C 2p) \) and the total DOS. The results are shown in Fig. 3(a) for \( Mn_4N \) and in Fig. 3(b) for \( Mn_4C \).

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 \( Mn(1) \) in part (ii). The \( 3d \) orbitals of \( Mn(1) \) mix little with \( 2p \) orbitals.
Table 1. The Slater-Koster(SK) integrals and the site energies for Mn$_4$N and Mn$_4$C (in unit of Ryd).

<table>
<thead>
<tr>
<th>SK integral</th>
<th>Mn$_4$N</th>
<th>Mn$_4$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t(ddd)$ Mn(I)-Mn(II)</td>
<td>-0.03</td>
<td>-0.035</td>
</tr>
<tr>
<td>$t(ddd)$ Mn(II)-Mn(II)</td>
<td>0.025</td>
<td>0.033</td>
</tr>
<tr>
<td>$t(ddd)$ Mn(II)-N</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$t(pdo)$ Mn(I)-Mn(II)</td>
<td>0.12</td>
<td>0.118</td>
</tr>
<tr>
<td>$t(pdo)$ Mn(II)-C</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>$E_s$ Mn(I)</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>$E_x$ Mn(I)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$E_z(x^2-y^2)$ Mn(I)</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>$E_z(3z^2-r^2)$ Mn(I)</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>$E_p$ N</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>$E_p$ C</td>
<td>0.28</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Table 2. The magnetic moment $m$ [$\mu_0$], the DOS [states/(Ryd·atom) or states/(Ryd·unit cell)], the exchange energy $I$ [Ryd] and the exchange splitting $\Delta$ [Ryd] in the ferrimagnetic state of Mn$_4$N. The arrows $\uparrow$ and $\downarrow$ denote the up-spin and the down-spin states, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$m$</th>
<th>$N(E_F)$</th>
<th>$I$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(I)</td>
<td>3.9</td>
<td>11(\uparrow)</td>
<td>0.063</td>
<td>0.248</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8(\downarrow)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>-0.88</td>
<td>27(\uparrow)</td>
<td>0.048</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14(\downarrow)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.07</td>
<td>0.65(\uparrow)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.46(\downarrow)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>1.3</td>
<td>140</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$_4$C is similar to Mn$_4$N except that the part (i) region of Mn$_4$C moves to the higher energy side compared with Mn$_4$N.

To calculate the DOS for the ferrimagnetic state of Mn$_4$N, the exchange splittings $\Delta_i$ are introduced for up and down spin states of the 3$d$ orbitals at Mn(I) and Mn(II) sites. We have assumed $\Delta_i$ is independent of the orbital $m$ and determined its value so as to reproduce the observed Mn moments of pure Mn$_4$N. The total and partial DOS's calculated for the ferrimagnetic state of Mn$_4$N are shown in Fig. 4.

The exchange splittings $\Delta_i$, the values of the DOS's at $E_F$ and the magnetic moments $m_i$ (in unit of $\mu_0$) 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 3$d$ and the N 2$p$ orbitals. From the values of the exchange splitting $\Delta_i$ 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. By using the total DOS at $E_F$, the coefficient of the electronic specific heat $\gamma$ of Mn$_4$N is estimated to be 24 mJK$^{-2}$mol$^{-1}$. On the other hand, the observed value of $\gamma$ is $42\pm2$ mJK$^{-2}$mol$^{-1}$.$^{11}$ Then, the mass enhancement factor due to electron correlation and/or electron-phonon interaction is evaluated to be $\lambda=0.75$. 


(2) **Mixed compound Mn$_4$N$_{0.75}$C$_{0.25}$**

In the calculation of the DOS for the non-magnetic and the ferrimagnetic states of Mn$_4$N$_{0.75}$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$_4$N 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 $t(pdo)$ etc., the orbital energies of the 3d or 2p states and the exchange splitting $\Delta_n$, 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 $t(\sigma \sigma)$, $t(\sigma \pi)$ and $t(\pi \pi)$ as those determined for Mn$_4$N. Furthermore, we have assumed the same exchange splitting as for Mn$_4$N.

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

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

<table>
<thead>
<tr>
<th></th>
<th>$m$</th>
<th>$N(E_F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)</td>
<td>3.9</td>
<td>12 ($\uparrow$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3 ($\downarrow$)</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>-0.95</td>
<td>26 ($\uparrow$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16 ($\downarrow$)</td>
</tr>
<tr>
<td>total</td>
<td>1.1</td>
<td>141</td>
</tr>
</tbody>
</table>
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Fig. 6. The total and partial DOS's for the mixed compound $\text{Mn}_4\text{Ni}_{0.25}\text{C}_{0.25}$: (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 $\text{Mn}_4\text{Ni}_{1-x}\text{C}_x$ ($x = 0, 0.25$ 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$_4$N$_{1-x}$C$_x$ ($x = 0$, 0.25 and 1). Calculations for $x = 1$, i.e. for pure Mn$_4$C have been performed by using the same exchange splittings as those of Mn$_4$N. In the mixed compound Mn$_4$N$_{0.75}$C$_{0.25}$, the calculated magnetic moment of Mn(I) is found to be almost unchanged compared with that of Mn$_4$N 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) 3$d$ 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$_4$N, which is reasonable assumption for low concentration of C atoms.

References