

## Band calculations for $\text{Mn}_4\text{N}$ and body-centred cubic Mn, fixing local spin directions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 1575

(<http://iopscience.iop.org/0953-8984/4/6/023>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:00

Please note that [terms and conditions apply](#).

## Band calculations for $Mn_4N$ and body-centred cubic Mn, fixing local spin directions

Shinpei Fujii†, Shoji Ishida† and Setsuro Asano‡

† Department of Physics, Faculty of Science, Kagoshima University, Kagoshima 890, Japan

‡ Institute of Physics, College of Arts and Sciences, University of Tokyo, Meguro-ku, Tokyo 153, Japan

Received 24 July 1991, in final form 25 September 1991

**Abstract.** We performed band calculations by the linear muffin-tin orbital (LMTO) atomic sphere approximation (ASA) method for  $Mn_4N$  and BCC Mn using an exchange–correlation potential that depends on each of local spin directions at atomic spheres. We discussed the magnetic structure of  $Mn_4N$  on the basis of results for two prototypes among several models proposed experimentally for  $Mn_4N$ . We discussed the coexistence of ferromagnetic and antiferromagnetic states in BCC Mn.

### 1. Introduction

Numerous spin-polarized band calculations based on the local-spin-density (LSD) approximation have been performed by the use of a constraint of a fixed total number of electrons in a given volume. A detailed study of magnetic properties of materials has been made possible by two modified versions of the usual spin-polarized band calculation. One is called the fixed-spin-moment procedure [1], which finds the ground-state energy of an electron's system under two constraints: a constraint that the spin moment of the system is fixed to a given value, as well as a fixed-electron-number constraint. The other is used to single out the correct ground state from several possible spin arrangements [2]. An essential feature of this procedure is the use of an exchange–correlation potential that varies from site to site in a crystal. Thus, the band calculation is performed under two constraints: a constraint that the spin moment on a site is fixed to a given local direction besides the usual constraint of the total number of electrons in a given volume. We call this procedure 'the local-fixed-spin-direction procedure'. The fixed-spin-moment procedure has been discussed in detail, for example, by Marcus and Moruzzi [3] and applied to the magnetic transitions of 3d transition metals. The local-spin-fixed-direction procedure has been formulated by Kübler *et al* [2] and applied to non-collinear antiferromagnetic  $\gamma$ -FeMn,  $RhMn_3$  and  $PtMn_3$ . In this paper we applied the local-spin-direction procedure to  $Mn_4N$  and BCC Mn.

The structure of  $Mn_4N$  is composed of Mn atoms at the corner and face-centred positions and a nitrogen atom at the body-centred position in a cubic lattice.  $Mn_4N$  has a total magnetic moment of  $1.2\mu_B$  per unit cell. To explain this low value, various magnetic structures have been proposed; they are summarized in table 1

**Table 1.** Calculated total energies and magnetic moments of  $Mn_4N$ : case (1),  $R_1 = R_2 = R_3$ ; case (2),  $R_1 = R_2, R_3/R_1 = 0.79$ ; case (3),  $R_1 : R_2 : R_3 = 1.000 : 0.968 : 0.782$ .  $E_{tot}$  and  $M_{tot}$  are the difference in total energy and the total magnetic moment, respectively.  $Q_{max}$  is the maximum absolute value of differences between the charge of a neutral atom and that in a sphere of the atom.  $M_i$  ( $i = 1, 2, 3, 4$ ) are the magnetic moments.

Case	$E_{tot}$ (mRyd/unit cell)	$M_i(\mu_B)$				$M_{tot}$ ( $\mu_B$ /unit cell)	$Q_{max}$
		$Mn_1$ (0, 0, 0)	$Mn_2$ ( $\frac{1}{2}, \frac{1}{2}, 0$ )	$Mn_3$ ( $\frac{1}{2}, 0, \frac{1}{2}$ )	$Mn_4$ ( $0, \frac{1}{2}, \frac{1}{2}$ )		
(1) $Mn_4N$ -a	14.7	+3.74	+2.03	-1.94	-1.94	+1.89	1.56
(1) $Mn_4N$ -b	0.0	+3.75	-0.77	-0.77	-0.77	+1.44	1.53
(2) $Mn_4N$ -a	15.6	+3.50	+2.11	-2.48	-2.48	+0.65	0.21
(2) $Mn_4N$ -b	0.0	+3.60	-0.83	-0.83	-0.83	+1.11	0.25
(3) $Mn_4N$ -a	14.2	+3.46	+2.09	-2.50	-2.50	+0.55	0.04
(3) $Mn_4N$ -b	0.0	+3.59	-0.80	-0.80	-0.80	+1.19	0.08
Experimental data[5]		+3.5	-0.77	-0.77	-0.77	+1.19	
Experimental data[4]		+3.85	-0.90	-0.90	-0.90	+1.15	

of the paper by Takei *et al* [4]. The proposed models are all ferrimagnetic spin arrangements and classified into two prototypes. One is a model where a corner moment and a face-centred moment are antiparallel to the other two face-centred moments (designated  $Mn_4N$ -a). The other is a model where a corner moment is antiparallel to the three face-centred moments (designated  $Mn_4N$ -b). This motivates us to carry out the calculation for  $Mn_4N$  by a local-fixed-spin-direction procedure because this procedure is suitable for determining the correct spin arrangement. An additional motivation is as follows. Because neutron diffraction experiments [4, 5] confirmed the spin arrangement of the  $Mn_4N$ -b type, we can know whether or not the calculation gives a consistent result with experiment.

Previously, Fujii *et al* [6] performed the usual spin-polarized band calculations of BCC Mn as a function of lattice constant and showed that the magnetic state of BCC Mn changes from paramagnetic to antiferromagnetic through ferromagnetic on increase in the lattice constant. However, they did not discuss the coexistence of ferromagnetic and antiferromagnetic states. Although the fixed-spin-moment procedure is usually used to analyse such a coexistence region, we show that a local-fixed-spin-direction procedure may also be applicable to such a problem.

We performed total-energy band calculations by the LMTO ASA method [7] using a muffin-tin potential. The exchange-correlation potential was treated by the LSD approximation, in the von Barth-Hedin form as parametrized by Janak *et al* [8]. The eigenvalue calculation was performed using 125  $k$ -points for  $Mn_4N$  and 35  $k$ -points for BCC Mn in the irreducible Brillouin zone, where the adopted unit cells are as follows: a cubic unit cell with a point group  $D_{2h}$  for  $Mn_4N$  and a CsCl unit cell for BCC Mn. The density of states (DOS) was obtained by the tetrahedral integration method [9].

## 2. Results and discussion

### 2.1. $Mn_4N$

In the LMTO ASA calculation for an open structure such as  $Mn_4N$ , it is better to

introduce empty spheres to construct a close packing with the atomic and empty spheres. Furthermore, errors due to the ASA may be reduced by including 'combined corrections'. However, we do not introduce empty spheres and we neglect the combined corrections in the present calculations. An overlap between two spheres with the radii  $S_1$  and  $S_2$  is defined as  $(S_1 + S_2 - d)/S_i$  ( $i = 1, 2$ ), where  $d$  is the distance of the two spheres. When the radii of the constituent atoms in  $Mn_4N$  are the same, the values of the overlaps are 0.62 between Mn and N, and 0.05 between Mn and Mn. This indicates that the ASA without empty spheres is not a reasonable approximation because the overlap must in principle be kept as low as possible and there is a guiding principle that the overlap is limited to 30% [10]. One of the present authors [11] showed that good agreement between the experimental and calculated results was obtained with respect to the magnetic moments and the hyperfine fields for  $Fe_4N$ , although the overlap between Fe and N was more than 0.3. Therefore, we also choose the radii for  $Mn_4N$  in the same manner as  $Fe_4N$ . As is shown later, if we choose atomic radii leading to spheres of neutral charge, we shall obtain excellent agreement with experiment with respect to the magnetic moments and the spin structure for  $Mn_4N$ , although the present calculations are preliminary to more accurate calculations.

We consider the following three cases with different combinations of sphere radii for  $Mn_4N$  with the lattice constant  $a = 3.865 \text{ \AA}$  [4]. In case (1), all the sphere radii  $R_1$ ,  $R_2$  and  $R_3$  have the same value, where  $R_1$ ,  $R_2$  and  $R_3$  mean sphere radii for Mn at a corner position, Mn at a face-centred position and N at a body-centred position, respectively. In case (2),  $R_1$  is equal to  $R_2$  but different values are permitted for  $R_1$  and  $R_3$ . In case (3),  $R_1$ ,  $R_2$  and  $R_3$  have different values. The sphere radii in cases (2) and (3) are determined from paramagnetic calculations so as to minimize the difference between the total charge of a neutral atom and that in a sphere of the atom. In case (2) the result  $R_3/R_1 = 0.79$  is obtained by changing the ratio  $R_3/R_1$  from 0.60 to 0.90 at regular intervals of 0.01 and the overlaps are as follows: less than 0.58 between Mn and N, and 0.12 between Mn and Mn. In case (3) the result  $R_1 : R_2 : R_3 = 1.000 : 0.968 : 0.782$  is obtained by using a trial-and-error method and the overlaps are as follows: less than 0.58 between Mn and N, and less than 0.16 between Mn and Mn.

Using those sphere radii we performed spin-polarized calculations for two spin arrangements  $Mn_4N$ -a and  $Mn_4N$ -b. The  $Mn_4N$ -a type means the spin arrangement where a corner moment and a face-centred moment are antiparallel to two other face-centred moments. The  $Mn_4N$ -b type means the spin arrangement where a corner moment is antiparallel to the three face-centred moments. In both types the moment of a nitrogen atom is defined to be perpendicular to the moments of Mn atoms. We list in table 1 the calculated total energies and magnetic moments, together with  $Q_{\max}$ , the maximum absolute value of differences between the total charge of a neutral atom and that in a sphere of the atom. Furthermore, in table 1 we also give the neutron diffraction experimental data which confirm the  $Mn_4N$ -b type. Since the magnetic moment of a nitrogen atom is less than  $0.001\mu_B$ , the value is not listed in table 1. This table shows that in any of three cases the total energy of  $Mn_4N$ -b is about 15 mRyd lower than that of  $Mn_4N$ -a, although the  $Q_{\max}$ -values are significantly different for the three cases. Concerning the total magnetic moment per unit cell and moments of individual Mn atoms, the  $Mn_4N$ -b type of case (3), which has smaller  $Q_{\max}$ -values than the other two cases, gives excellent agreement with experiment. From the above-mentioned facts we concluded that the local-fixed-spin-

direction procedure gives a consistent result with experiment, at least in the case of  $\text{Mn}_4\text{N}$ , and in this case the charge neutrality in a sphere is an important factor.

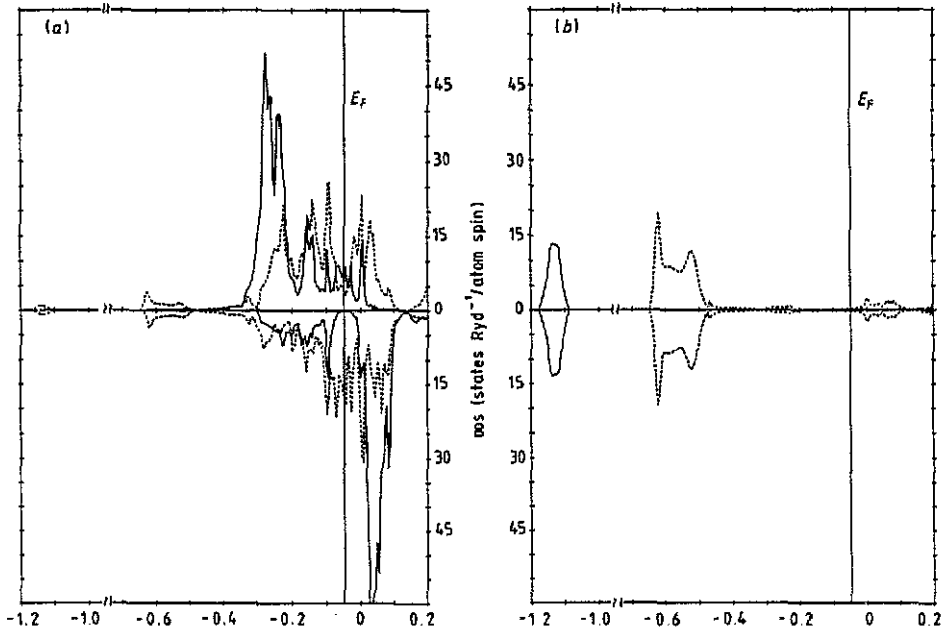


Figure 1. DOS curves of  $\text{Mn}_4\text{N-b}$  type in case (3): (a) d bands of Mn atoms - - -, Mn  $(0, 0, 0)$ ; - · -, Mn  $(\frac{1}{2}, 0, \frac{1}{2})$ ; (b) s (—) and p (---) bands of N atoms. In each figure, the DOS curves for up-spin (majority-spin) electrons are shown in the upper part and those for down-spin (minority-spin) electrons in the lower part. The Fermi level is indicated by the vertical full line.

We turn our attention to the DOS of the  $\text{Mn}_4\text{N-b}$  type in case (3) where the agreement between calculated results and experimental data is very good. We show in figure 1(a) the d DOS of Mn atoms and in figure 1(b) the s and p DOS of N atoms. In figure 1(a) we draw the DOS curve of each of two Mn atoms at the positions  $(0, 0, 0)$  and  $(\frac{1}{2}, 0, \frac{1}{2})$  in the cubic lattice. The two Mn atoms have the following different magnetic moment values:  $+3.59\mu_B$  and  $-0.80\mu_B$  for Mn atoms at  $(0, 0, 0)$  and  $(\frac{1}{2}, 0, \frac{1}{2})$ , respectively (see table 1). Figure 1(a) shows that there is a significant difference between the two DOS curves of Mn atoms. The DOS curve of Mn at  $(0, 0, 0)$  has a giant peak in each spin state and the peak of the up-spin (majority-spin) electrons is located below the Fermi level, while the peak of the down-spin (minority-spin) electrons is above the Fermi level. That is, the former peak is occupied and the latter peak unoccupied. On the other hand, the DOS curve of Mn at  $(\frac{1}{2}, 0, \frac{1}{2})$  has a structure with several fine peaks and is not a structure with a giant peak. The large difference between the magnetic moments of Mn atoms at  $(0, 0, 0)$  and  $(\frac{1}{2}, 0, \frac{1}{2})$  can be attributed to the above-mentioned difference between the two DOS curves of Mn atoms. Making a comparison of DOS curves of Mn and N atoms, we note, furthermore, the following fact. The existence of two small peaks which appear below  $-0.5$  Ryd in the DOS curve of Mn at  $(\frac{1}{2}, 0, \frac{1}{2})$  indicates hybridization between d bands of Mn atoms at  $(\frac{1}{2}, 0, \frac{1}{2})$  and s or p bands of N atoms. However, in

the DOS curve of Mn at (0, 0, 0) there is hardly anything to indicate hybridization.

## 2.2. BCC Mn

Previously, Fujii *et al* [6] showed that in the neighbourhood of a lattice constant of 2.95 Å the ground state of BCC Mn changed from a ferromagnetic state to an antiferromagnetic state with increase in lattice constant. However, they did not discuss the coexistence of ferromagnetic and antiferromagnetic states. We investigate whether or not the local-fixed-spin-direction procedure is suitable for analysing such a coexistent region by performing band calculations for BCC Mn with a CsCl unit cell. In the calculations, we consider the following three spin arrangements. First, a corner moment is parallel to a body-centred moment, i.e. a ferromagnetic arrangement. Second, a corner moment is antiparallel to a body-centred moment, i.e. an antiferromagnetic arrangement. Third, a corner moment and a body-centred moment are parallel to [011] and  $[0\bar{1}1]$ , respectively. This arrangement means that, in the  $z$  direction, one moment couples with another ferromagnetically, and in the  $y$  direction antiferromagnetically. Therefore, we consider the third arrangement as the coexistent state of ferromagnetic and antiferromagnetic states.

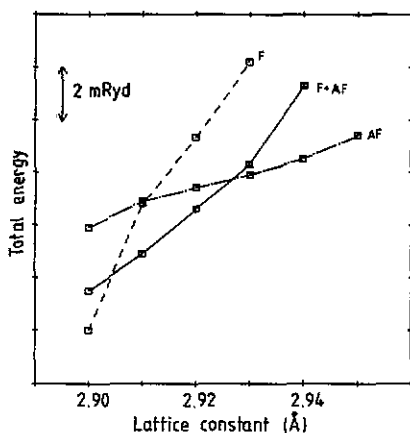


Figure 2. Comparison of total energies for three magnetic states: ferromagnetic (F) (---), antiferromagnetic (AF) (— · —) and mixture of both (F + AF) (—); □, calculated points.

We performed band calculations changing the lattice constant from 2.80 to 3.10 Å and figure 2 shows the results obtained. Figure 2 demonstrates that there is certainly a region where the coexistent state of ferromagnetic and antiferromagnetic states has the lowest total energy of the three different states. This indicates that the local-fixed-spin-direction procedure and the fixed-spin-moment procedure are suitable for analysing a problem where two or more magnetic states coexist in a narrow volume region. We feel that a procedure such as the former, but based on the principle of the latter procedure may be most suitable because the local-fixed-spin-direction procedure can deal with both collinear and non-collinear spin arrangements.

## Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan. The numerical calculations were performed on the

FACOM M-780 and VP-200 at Computer Center of Kyushu University and on the IBM-3081K at Information Processing Center of Kagoshima University.

## References

- [1] Schwartz K and Mohn P 1984 *J. Phys. F: Met. Phys.* **14** L129
- [2] Kübler J, Höck K-H, Sticht J and Williams A R 1988 *J. Phys. F: Met. Phys.* **18** 469
- [3] Marcus P M and Moruzzi V L 1988 *J. Appl. Phys.* **63** 4045
- [4] Takei W J, Heikes R R and Shirane G 1962 *Phys. Rev.* **125** 1893
- [5] Takei W J, Shirane G and Frazer B C 1960 *Phys. Rev.* **119** 122
- [6] Fujii S, Ishida S and Asano S 1991 *J. Phys. Soc. Japan* **60** 1193
- [7] Andersen O K, Jepsen O and Glotzel D 1985 *Proc. Int. School of Physics 'Enrico Fermi' Course vol 89*, ed F Bassani, F Fumi and M P Tosi (Amsterdam: North-Holland) p 59
- [8] Janak J K, Moruzzi V L and Williams A R 1975 *Phys. Rev. B* **12** 1257
- [9] Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1963  
Rath J and Freeman A J 1975 *Phys. Rev. B* **11** 2109
- [10] Andersen O K, Jepsen O and Sob M 1987 *Electronic Band Structure and its Applications (Lecture Notes in Physics 287)* ed M Yussouff (Berlin: Springer) p 15
- [11] Ishida S 1992 *J. Magn. Magn. Mater.* at press