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Structural, electronic and magnetic properties of MnB_2

R MASROUR[1,2,*], E K HLIL[3], M HAMEDOUN[4], A BENYOUSSEF[2,4,5], O MOUNKACHI[4] and H EL MOUSSAOUI[4]

[1]Laboratory of Materials, Processes, Environment and Quality, Cady Ayyed University, National School of Applied Sciences, 63, 46000 Safi, Morocco
[2]LMPHE (URAC 12), Faculty of Science, Mohammed V-Agdal University, Rabat, Morocco
[3]Institut Néel, CNRS et Université Joseph Fourier, BP 166, F-38042 Grenoble Cedex 9, France
[4]Institute of Nanomaterials and Nanotechnologies, MAScIR, Rabat, Morocco
[5]Hassan II Academy of Science and Technology, Rabat, Morocco

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Abstract. **The self-consistent *ab-initio* calculations, based on density functional theory approach and using the full potential linear augmented plane wave method, are performed to investigate both electronic and magnetic properties of the MnB_2 compounds. Polarized spin and spin–orbit coupling are included in calculations within the framework of the ferromagnetic state between two adjacent Mn atoms. Magnetic moment considered to lie along the (001) axes are computed. The antiferromagnetic and ferromagnetic energies of MnB_2 systems are obtained. Obtained data from *ab-initio* calculations are used as input for the high-temperature series expansions (HTSEs) calculations to compute other magnetic parameters. The exchange interactions between the magnetic atoms Mn–Mn in MnB_2 are established by using the mean field theory. The HTSEs of the magnetic susceptibility with the magnetic moments in MnB_2 (m_{Mn}) through Ising model is given. The critical temperature T_C (K) is obtained by HTSEs applied to the magnetic susceptibility series combined with the *Padé* approximant method. The critical exponent γ associated with the magnetic susceptibility is deduced as well.**

Keywords. **MnB_2 compound; electronic and magnetic structures; magnetic moment; DOS.**

1. Introduction

In recent years, much research has been carried out on the magnetic properties of intermetallic compounds incorporated in transition metals. The magnetic behaviour was found to depend sensitively on the nature of the transition metal involved, and on the local environment of the transition-metal atom within a given structure. The borides of transition metals show many interesting properties, such as high hardness, high melting point, thermodynamic stability and several of them are ferromagnetic at room temperature. The magnetic and electronic structures of several X_2B nanoparticles such as Co_2B, Mn_2B and W_2B have already been discussed in many papers previously.[1–9] The magnetic properties of the MnB_2 and CrB_2 are explained in reference.[10] Stadler *et al*[5] had studied the electronic structures of WB, W_2B and W_2B_5 by using the soft X-ray emission and adsorption spectroscopic techniques and the density functional theory (DFT) calculations. The calculated local magnetic moments are 1.962 and 1.182 μ_B for Fe_2B and Co_2B, respectively. They are very close to the values of Fe_3B and Co_3B.[7] Kanomata *et al*[11] studied the magneto-volume effect of Co_2B; they found that the saturation moment at 4.2 K was 1.56 μ_B/f.u. Shein-Igor *et al*[12] have performed *ab-initio* calculations to study the electronic and magnetic properties of X_3B (X = Fe, Co and Ni). They conclude that Ni_3B and Ni_3C are both paramagnetic. Fe_3B and Co_3B are both ferromagnetic, with the evaluated magnetic moment value of 1.97 μ_B/Fe and 1.18 μ_B/Co, respectively.[13] The nominal charges carried by metal atoms in X_2B crystal cannot be used directly to compare with reference,[8] and in fact, X_2B compounds studied in this paper are metallic in nature and the Mulliken population method is ill defined in this case. The structural, elastic, electronic and magnetic properties of Mn_3ZnC and Mn_3GeC are reported in reference.[14]

In this paper, three approaches—self-consistent *ab-initio* calculations, mean field and temperature series expansions (HTSEs) calculations—are used to shed light on the magnetic structure. Firstly, full potential linear augmented plane wave (FLAPW) calculations based on DFT principle are performed on MnB_2 compounds. Appropriate polarized spin and spin–orbit coupling as well as ferromagnetic state are considered. Considering computed magnetic moment from FLAPW calculations as input data, we have used the mean field theory to find the first, second and third exchange interactions between the magnetic atoms Mn–Mn in MnB_2 compound. The ferro- and antiferromagnetic energies are computed. The HTSEs of the magnetic susceptibility of MnB_2 through Ising model combined with the *Padé* approximant[15] is studied up to *ten*th order series in ($\beta = 1/k_BT$). Finally, the critical temperature is deduced.

*Author for correspondence (rachidmasrour@hotmail.com)

2. Electronic structure calculations

We used the FLAPW method[16] which performs DFT calculations using the local density approximation. The Kohn–Sham equation and energy functional were evaluated consistently using the FLAPW method. For this method, the space was divided into the interstitial and the non-overlapping muffin tin spheres centred on the atomic site. The employed basis function inside each atomic sphere was a linear expansion of the radial solution of a spherically potential multiplied by spherical harmonics. In the interstitial region the wave function was taken as an expansion of plane waves and no shape approximation for the potential was introduced in this region which is consistent with the full potential method. The core electrons were described by atomic wave functions which were solved relativistically using the current spherical part; the valence electrons were also treated relativistically in our case. These FLAPW calculations were performed with the crystal structure parameters reported in reference.[17] Here, polarized spin, spin–orbit coupling as well as the ferromagnetic state were considered for Mn ($3d^5 4s^2$) adjacent compounds. The Mn magnetic moments were considered to lie along the (001) axis[18] as shown in figure 1.

3. Material and methods

3.1 *Mean field theory*

The Hamiltonian of the system is given by

$$H = -J(\mathrm{Mn}-\mathrm{Mn}) \sum_{<i,j>} m_{i\mathrm{Mn}} m_{j\mathrm{Mn}} - h \sum_{i} m_{i\mathrm{Mn}}, \qquad (1)$$

where h is the external magnetic field, J(Mn–Mn) the first exchange interactions between the (Mn–Mn) atoms in MnB_2 compound (see figure 1). m_i is the magnetic moment of Mn ion located on the ith site. The mean field approximation used in reference[19] leads to simple relations between exchange integrals J(Mn–Mn) and the critical temperature T_C (K). The expression obtained is

$$J\ (\mathrm{K}) = \frac{T_C\ (\mathrm{K})}{m\ (m+2)}, \qquad (2)$$

Where k_B is Boltzmann's constant, $m = 2.38\ \mu_B$ (μ_B is the Bohr magnetron).

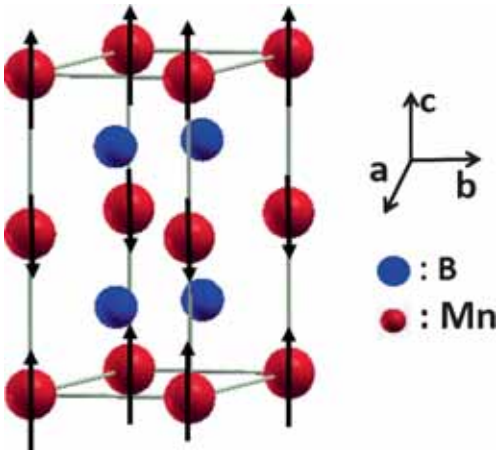

Figure 1. Magnetic structure of MnB_2 compounds as used in calculations.

3.2 *High-temperature series expansion*

The theoretical method used in this study has been developed in previous papers.[20,21] We consider a ferromagnetic cubic system with magnetic moment m_{Mn}.

The statistics of our spin system are studied using the HTSE whose starting point is the expansion of the correlation function

$$\langle m_i m_j \rangle = \frac{Trm_i m_j e^{-\beta H}}{Tre^{-\beta H}}$$

between spins at sites i and j, in powers of β:[22]

(i)

$$Trm_i m_j e^{-\beta H} = \sum_{l}^{\infty} \frac{(-1)^m}{m!} Trm_i m_j H^m \beta^m = \sum_{m=0}^{\infty} a_m \beta^m, \qquad (3)$$

with

$$a_m = \frac{(-1)^m}{m!} Trm_i m_j H^m,$$

which can be written in the form

$$a_m = \frac{(-1)^m}{m!} \left\langle m_i m_j H^m \right\rangle = \frac{(-1)^m}{m!} \nu_m, \qquad (4)$$

where $\nu_m = \langle m_i m_j H^m \rangle$ and $\langle \cdots \rangle$ the average is conducted at infinite temperature ($\beta = 0$)

(ii)

$$Z = Tre^{-\beta H} = \sum_{n=0}^{\infty} b_n \beta^n \qquad (5)$$

with

$$b_n = \frac{(-1)^n}{n!} \mu_n, \qquad (6)$$

where $\mu_m = \langle H^m \rangle_{T=\infty}$

The correlation function is

$$\left\langle m_i m_j \right\rangle_T = \frac{\sum_{m=0}^{\infty} a_m \beta^m}{\sum_{n=0}^{\infty} b_n \beta^n}. \qquad (7)$$

The final expression of the correlation function is

$$\gamma_{ij} = \langle m_i m_j \rangle_T = \sum_{l=0}^{\infty} \frac{(-1)^l}{l!} \alpha_l \beta^l, \qquad (8)$$

where $\beta = 1/k_B T$ (k_B being Boltzmann's constant).

With

$$\alpha_l = \nu_l - \sum_{k=0}^{l-1} C_k^l \alpha_k \mu_{l-k}, \quad \nu_m = \left\langle \vec{\sigma}_i \vec{\sigma}_j H^m \right\rangle_{T=\infty}$$

and

$$\mu_m = \left\langle H^m \right\rangle_{T=\infty}.$$

In our case, we have to deal with nearest-neighbour coupling J_{ij}. The coefficient α_l should be expressed for each topological graph as given in reference.[23]

For the MnB_2 compound, we obtain the following function:

$$\chi(T) = \sum_{i,j} \langle m_i m_j \rangle_T = \sum_{l=0}^{\infty} \frac{(-1)^l}{l!} \alpha_l \beta^l \tag{9}$$

with

$$\alpha_l \approx (J_{sk_1}^{m_1} J_{k_2k_3}^{m_2} \ldots J_{k_w\perp}^{m_v})[\alpha_l].$$

The HTSE method is developed for the magnetic susceptibility $\chi(T)$ with arbitrary exchange interaction J. The 'weight' $[\alpha_l]$ of each graph is tabulated and given in reference.[24] The $k_1, k_2, \ldots, k_w$ represent the sites surrounding the sites i and j. The convergence of magnetic susceptibility was found to be quite rapid and we expect that the result will be accurate to within 1%

$$\chi(\beta) = \beta \sum_{n=0}^{m} \sum_{m=0}^{10} a_m^n x^{-n} \tag{10}$$

with $x = J/k_B T$ is the reduced temperature, β is Boltzmann's constant. The coefficients a_m^n, given in magnetic susceptibility of MnB_2 compound, are tabulated in table 1 for Ising model.

The high-temperature series expansions of magnetic susceptibility obtained in the present calculation are directly evaluated from the two rooted diagrams. The high-temperature series expansions of magnetic susceptibility could also be evaluated from the free energy to second order in h and taking the derivative of the result twice with respect to the field.

4. Results and discussions

The density of state (DOS) of MnB_2 deduced from band structure calculations is reported in figure 2. Here, the Fermi level is taken as reference. This DOS is dominated by the Mn atom contributions taking place in both occupied states at negative energies and unoccupied states localized at positive energies. As seen, this DOS is symmetrical with respect to energy axis, pointing out that magnetic moments carried by Mn atoms are antiferromagnetically ordered.

In addition, the l-decomposed DOS of s, p and d like states are computed and reported in figures 3 and 4. They provide a more detailed picture and allow concluding that both Mn

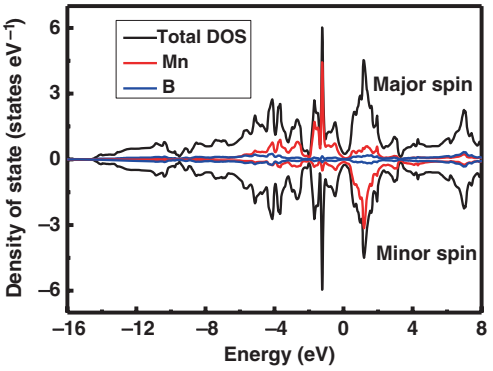

Figure 2. Total DOS, Mn DOS and B DOS from FLAPW calculations.

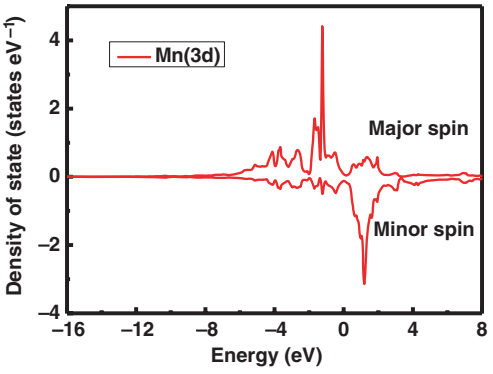

Figure 3. l-Decomposed DOS 3d like-states of Mn in MnB_2 from FLAPW calculations.

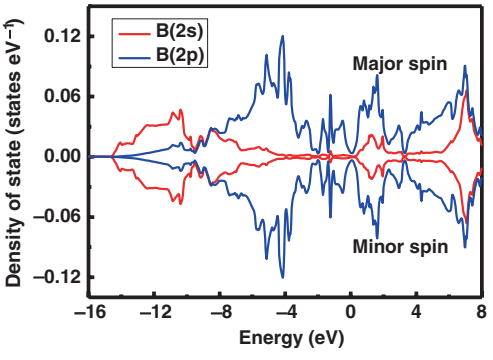

Figure 4. l-Decomposed DOS of 2s and 2p like states of B in MnB_2 from FLAPW calculations.

Table 1. Series coefficients for the high-temperature developed susceptibility series bcc lattices for MnB_2 compounds for Ising model with magnetic moment $m_{Mn} = 2.38\ \mu_B$.

a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}
1	−57.56	−218.728	−815.049	−2999.735	−109,49.999	−39,739.483	−143,598.368	−517,156.431	−1,857,528.351	−6,657,390.324

Table 2. Critical temperature, exchange interactions, ferro- and antiferromagnetic energies and the critical exponents of MnB_2 for Ising model.

Compound	T_C (K), HTSE	Magnetic moment, this work	Magnetic moment[18]	T_C (K), experiment[18]	J(Mn–Mn) (K)	Critical exponents, γ	E_{FM} (K), *ab-initio* calculations	E_{AFM} (K), *ab-initio* calculations
MnB_2	158	2.38	2.3	150	−14.39	1.39 ± 0.01	$-0.1051780122 \times 10^{13}$	$-0.1051782985 \times 10^{13}$

contributions have mainly a character of 3d band while the projected DOS on B ($2s^2 2p^1$) atom is dominated by contributions from 2s and 2p bands. Magnetic moment of Mn is computed as well and found equal to 2.38 μ_B (see table 2). This value is near to those obtained by Aronsson.[17] The transitions from antiferromagnetic state to paramagnetic state are promoted by the following reasons. Firstly, the metallic X–X bonds are weakened and the X–B bonds are enhanced, and which result in loss of exchange energy of X–X bonds. Secondly, electrons in 3d bands are increased and can reduce the magnetic moment of metal atoms greatly. We have used the magnetic measurement reported in reference[17] to calculate the exchange integrals J(Mn–Mn) by using the mean field theory. The obtained values are given in table 2. The HTSE extrapolated with the Padé approximants method is known to be a convenient method to provide valid estimate of the critical temperatures for real system. By applying this method to the magnetic susceptibility, $\chi(T)$, we have estimated the critical temperature T_C (K) for MnB_2. The Padé approximant analysis of the magnetic susceptibility is used to estimate the critical temperature of MnB_2 compounds. The critical temperature corresponds to the simple pole of $[\chi]$. The obtained values are given in table 2. The critical exponent γ associated with the magnetic susceptibility $\chi \approx (T - T_C)^{-\gamma}$ is computed for different values of Padé approximant for Ising model (see table 2).

5. Conclusions

FLAPW calculations were performed to investigate both electronic and magnetic structures for MnB_2 compound. This proves that the DOS of Mn atoms originate essentially from contributions of 3d bands while the projected DOS on B atoms is dominated by contributions from 2s and 2p bands. Magnetic moments carried by Mn atoms were computed as well and used as input data for HTSE's calculations. The magnetic properties of spin ferromagnetic Ising model on MnB_2 compounds using the high-temperature series expansions of magnetic susceptibility are investigated. The critical temperature T_C (K) is estimated from the divergence of the magnetic susceptibility with an exponent. All values are comparable with those reported in references[25,26] and fit with the universality hypothesis.[26]

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