Structural, electronic and magnetic properties of MnB$_2$

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MS received 22 May 2014; accepted 24 February 2015

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$_2$ ($m_{\text{Mn}}$) 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 $\gamma$ 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$_2$B nanoparticles such as Co$_2$B, Mn$_2$B and W$_2$B have already been discussed in many papers previously. The magnetic properties of the MnB$_2$ and CrB$_2$ are explained in reference. Stadler et al. had studied the electronic structures of WB, W$_2$B and W$_2$B$_5$ 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 $\mu_B$ for Fe$_2$B and Co$_2$B, respectively. They are very close to the values of Fe$_2$B and Co$_2$B. Kanomata et al. studied the magneto-volume effect of Co$_2$B; they found that the saturation moment at 4.2 K was 1.56 $\mu_B$/f.u. Shein-Igor et al. have performed ab-initio calculations to study the electronic and magnetic properties of X$_2$B

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2. Electronic structure calculations

We used the FLAPW method\(^\text{16}\) 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\(^\text{17}\). 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\(^\text{18}\) as shown in figure 1.

3. Material and methods

3.1 Mean field theory

The Hamiltonian of the system is given by

\[ H = -J_{\text{Mn–Mn}} \sum_{i<j} m_i m_j - h \sum_i m_i, \]

where \( h \) is the external magnetic field, \( J_{\text{Mn–Mn}} \) 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 \( i \)th site. The mean field approximation used in reference\(^\text{19}\) leads to simple relations between exchange integrals \( J_{\text{Mn–Mn}} \) and the critical temperature \( T_C \) (K). The expression obtained is

\[ J (K) = \frac{T_C (K)}{m (m + 2)}, \]

where \( k_B \) is Boltzmann’s constant, \( m = 2.38 \mu_B \) (\( \mu_B \) is the Bohr magnetron).

3.2 High-temperature series expansion

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

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

\[ \langle m_im_j \rangle = \text{Tr} m_im_j e^{-\beta H} \]

between spins at sites \( i \) and \( j \), in powers of \( \beta \)\(^\text{22}\):

(i)

\[ \text{Tr} m_i m_j e^{-\beta H} = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \text{Tr} m_i m_j H^m \beta^m = \sum_{m=0}^{\infty} a_m \beta^m, \]

with

\[ a_m = \frac{(-1)^m}{m!} \text{Tr} m_i m_j H^m, \]

which can be written in the form

\[ a_m = \frac{(-1)^m}{m!} \langle m_i m_j H^m \rangle = \frac{(-1)^m}{m!} \nu_m, \]

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

(ii)

\[ Z = \text{Tr} e^{-\beta H} = \sum_{n=0}^{\infty} b_n \beta^n \]

with

\[ b_n = \frac{(-1)^n}{n!} \mu_n, \]

where \( \mu_m = \langle H^m \rangle_{T=\infty} \).

The correlation function is

\[ \langle m_i m_j \rangle_T = \frac{\sum_{m=0}^{\infty} a_m \beta^m}{\sum_{n=0}^{\infty} b_n \beta^n}. \]

The final expression of the correlation function is

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

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

![Figure 1. Magnetic structure of MnB\(_2\) compounds as used in calculations.](image)
With
\[ \alpha_i = v_i - \sum_{k=0}^{l-1} C^l_k \mu_{l-k}, \quad v_m = \langle \tilde{\sigma}_i \tilde{\sigma}_j H^m \rangle_{T=\infty} \]
and
\[ \mu_m = \langle H^m \rangle_{T=\infty}. \]

In our case, we have to deal with nearest-neighbour coupling \( J_{ij} \). The coefficient \( \alpha_l \) should be expressed for each topological graph as given in reference.\(^\text{23}\) For the MnB\(_2\) compound, we obtain the following function:
\[ \chi(T) = \sum_{i,j} \langle \mu_{ij} \rangle_{T=\infty} \sum_{l=0}^{\infty} \frac{(-1)^l}{l!} \alpha_l \beta^l \]
with
\[ \alpha_l \approx (J_{m_1} J_{m_2} \ldots J_{m_{\perp}}) [\alpha_l]. \]

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.\(^\text{24}\) 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%
\[ \chi(\beta) = \beta \sum_{n=0}^{m} \sum_{m=0}^{10} a_n^m x^{-n} \]
with \( x = J/k_B T \) is the reduced temperature, \( \beta \) is Boltzmann’s constant. The coefficients \( a_n^m \), 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

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**Table 1.** Series coefficients for the high-temperature developed susceptibility series bcc lattices for MnB\(_2\) compounds for Ising model with magnetic moment \( m_{\text{Mn}} = 2.38 \mu_B \).

<table>
<thead>
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<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
<th>( a_5 )</th>
<th>( a_6 )</th>
<th>( a_7 )</th>
<th>( a_8 )</th>
<th>( a_9 )</th>
<th>( a_{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-57.56</td>
<td>-218.728</td>
<td>-815.049</td>
<td>-2999.735</td>
<td>-109.4999</td>
<td>-39,739.483</td>
<td>-143,598.368</td>
<td>-517,156.431</td>
<td>-1,857,528.351</td>
<td>-6,657,390.324</td>
</tr>
</tbody>
</table>
contributions have mainly a character of 3d band while the projected DOS on B ($2s^22p^1$) atom is dominated by contributions from 2s and 2p bands. Magnetic moment of Mn is computed as well and found equal to 2.38 $\mu_B$ (see table 2). This value is near to those obtained by Aronsson. 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 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 $\gamma$ 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 and fit with the universality hypothesis.

References

6. Xiao B et al 2008 Physica B 403 1723