PAPER

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Covalent magnetism, exchange interactions and anisotropy of the high temperature layered antiferromagnet MnB_2

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Abstract

The investigation of the electronic structure and magnetism for the compound MnB_2 with crystal structure type AlB_2 has been revisited to resolve contradictions between various experimental and theoretical results present in the literature. We find that MnB_2 exhibits an interesting example of a Kübler's covalent magnetism (Williams *et al* 1981 *J. Appl. Phys.* **52** 2069). The covalent magnetism also appears to be the source of some disagreement between the calculated values of the magnetic moments and those given by neutron diffraction experiments. We show that this shortcoming is due to the atomic sphere approximation applied in earlier calculations. The application of the disordered local moment approach and the calculation of the inter-atomic exchange interactions within the Liechtenstein formalism reveal strong local moment antiferromagnetism with a high Néel temperature predicted from Monte Carlo simulations. A fully relativistic band structure calculation and then the application of the torque method yields a strong in-plane anisotropy of the Mn magnetic moments. The agreement of these results with neutron diffraction studies rules out any possible weak itinerant electron magnetism scenarios as proposed earlier for MnB_2.

(Some figures may appear in colour only in the online journal)

1. Introduction

The transition metal diborides have been widely studied due to the large interest in their phase stability, refractory properties [2] and their potential for application as super-hard materials (see e.g. [3] for a review). Additional impetus to this studies has been added due to a search for superconductivity in metallic boride materials which revealed high temperature superconductivity in MgB_2 [4] with the same crystal structure as MnB_2 (figure 1). MnB_2 is a magnetic representative of metallic diborides and various investigations of the influence of magnetic Mn substitutions on the superconductivity of MgB_2 have been undertaken experimentally as well as theoretically [5–7].

The magnetic properties of MnB_2 has been subject to some controversy from an experimental point of view, ever since the earlier reports of weak itinerant electron ferromagnetism with a saturation magnetization at about 0.2 μ_B/Mn and a Curie temperature of about 140–150 K [8, 9]. Consequently neutron diffraction studies [10] have failed to resolve a weakly ferromagnetic component and suggest instead an antiferromagnetic phase with large atomic magnetic moments of 2.6 μ_B/Mn oriented parallel to the hexagonal crystal planes. Another investigation [11], which included an NMR study, also suggested antiferromagnetism without any ferromagnetic component and with a high Néel temperature of 760 K, whereas the weak ferromagnetism observed in earlier works can be only attributed to some secondary magnetic phase present in impure samples.

Last decade, first-principles electronic structure investigations of MnB_2 within the framework of density functional theory were undertaken several times. In their seminal paper on the electronic structure of the diborides, Vajeeston *et al* [12] show that the ferromagnetic state of MnB_2 has a

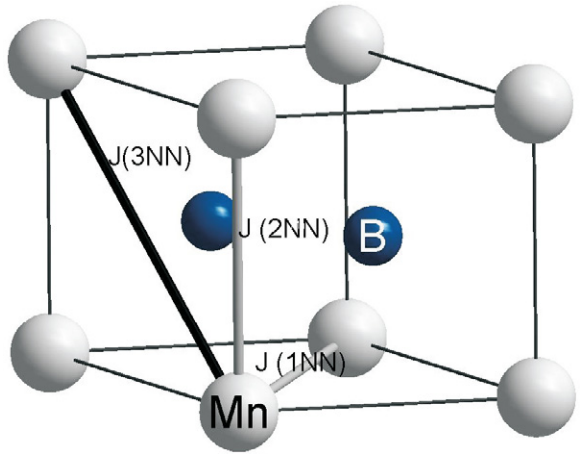

Figure 1. Hexagonal crystal structure of MnB_2; the first three NN pairs of Mn atoms are shown.

lower energy than a non-magnetic one with a moment of 1.6 μ_B/Mn within the local spin density approximation (LSDA). This result is similar to what has been derived for the ferromagnetic state in other LSDA calculations [3, 13] where the value of the moment is much larger than the weak ferromagnetic components observed in [8, 9]. However it also much smaller than the effective moment derived from magnetic susceptibility measurements and from neutron diffraction studies [10]. In [3] it was shown that the application of the general gradient approximation (GGA) gives a ferromagnetic moment of about 2 μ_B/Mn, which is, however, still much smaller than the experimental estimate. In addition it is known that GGA performs poorly with respect to LDA in predicting too large moments in transition metals. It is interesting that in [3, 12] only a ferromagnetic state has been investigated despite of the fact that other investigations [13] already suggested that antiferromagnetic order along the *c*-axis in LSDA leads to a lower energy than a ferromagnetic solution. The underestimation of the moment (for the ferromagnetic state, however) has been blamed [12] on covalent interplanar bonding between Mn and B atoms. The calculated [13] moments for the antiferromagnetic state are, at about 2 μ_B/Mn, still smaller than experimental ones. The attempt to explain the difference between the calculated values and experiment undertaken in [3, 13] by taking into account quantum effects in the Curie–Weiss law for the high T susceptibility is unlikely to succeed since there is direct evidence of local magnetic moments drawn from neutron diffraction experiments [10]. It thus appears that from *ab initio* calculations no definite conclusion can be drawn concerning the character of magnetism—itinerant or localized—or the nature of the stabilization of the antiferromagnetic phase or the sources of the disagreement between theory and experiment.

Since there exists a persistent confusion in the literature concerning the magnetic ground state of MnB_2 and other unresolved issues, we have performed a diversified first-principles study of magnetism in this material, combining full potential calculations using the linearized augmented plane wave (FLAPW) method and the Green function based Korringa–Kohn–Rostoker method based on the atomic sphere approximation (KKR-ASA). Application of the FLAPW has shown that the moments can be calculated in perfect agreement with experiment in the framework of the conventional LSDA. The previous problems were related to the use of ASA and the covalent character of the magnetism as described by Kübler *et al* [1] for the antiferromagnetic state of MnB_2. Our KKR-ASA calculations applying the disordered local moment (DLM) approach show that the magnetism of Mn in MnB_2 is essentially localized. We also calculate the inter-atomic exchange interactions and find a non-trivial origin of the stabilization of the antiferromagnetic ground state which allows us to predict a high Néel temperature.

Another important issue which motivates our study is the current interest in the mechanism of the magnetic anisotropy in high temperature antiferromagnetic materials with high Néel temperatures [14]. The anisotropy of antiferromagnets is a quantity which is not easily measurable; however, according to many theories (see e.g. [15]), it plays an important role in the mechanism of exchange bias. The applied materials most promising for application as pinning layers in exchange bias devices are layered antiferromagnetic alloys of Mn with 4d and 5d metals like MnIr, MnPt [14] etc. The high value of the magnetic anisotropy energy (MAE) was confirmed by *ab initio* calculations [16–18] as well as by some indirect experimental measurements [14]. The atom resolved calculation of the contributions to the MAE from spin–orbit coupling on different atomic species suggested [18] that in the case of the 3d–5d alloy of MnIr the dominant mechanism leading to the high MAE value is the spin–orbit coupling on the Ir sites. For other materials with layered antiferromagnetic structure and tetragonal $L1_0$ structure of MnX (X = Ni, Rh, Pd, Pt) it has been found [19] that the non-magnetic 3d and 4d elements also contribute to the total MAE on an equal footing with Mn. The contribution of Mn to the total MAE does not exceed 0.2 mRyd/atom over the MnX series and the total MAE is always determined by the combined effect of spin–orbit coupling (SOC) on Mn and the other d element. Although MnB_2 has a hexagonal structure, it is interesting to compare its MAE to the above mentioned MnX materials since a contribution of an sp element like B to the MAE is expected to be very small as compared to that of d metals. To achieve this goal and also to complete our study of the magnetism in MnB_2 we have calculated its MAE using the relativistic torque method as implemented in the FLAPW [20] method in a similar fashion to what has been done for various binary transition metal alloys [18, 21].

2. Calculational details

The electronic structure of MnB_2 compound has been calculated using the relativistic version of the full potential linear augmented plane wave (FP-LAPW) method [22] and in addition the scalar relativistic Korringa–Kohn–Rostoker Green function based method within the atomic sphere approximation (KKR-ASA) [23]. The SOC in the FLAPW calculation is included in a self-consistent second-variational

Table 1. Magnetic moment of MnB_2 per Mn atom in ferromagnetic (FM), layered antiferromagnetic (AFM), and disordered local moment (DLM) states calculated by different methods. ΔE(FM–AFM) is the calculated total energy difference between the FM and AFM states given per formula unit.

	FM m (μ_B/Mn)	AFM m (μ_B/Mn)	DLM m (μ_B/Mn)	ΔE(FM–AFM) (mRyd/f.u.)
KKR-ASA	1.67	1.98	1.67	7.22
FLAPW	2.35	2.59	—	9.09

procedure [20]. In both sets of calculations the exchange and correlation effects are treated within the framework of the local spin density approximation (LSDA) using the parametrization by von Barth and Hedin [24]. The calculations are done for the experimental lattice structure with lattice parameters $a = 3.01$ Å and $c/a = 1.01$ [10] of the AlB_2-type structure.

In the case of KKR-ASA calculations we used a spherical harmonic expansion up to $l_{max} = 3$ (spdf basis set). Multipole moment contributions to the non-spherical part of the electrostatic contribution to the one-electron potential inside the ASA spheres were also determined by carrying out the summation up to $l^M_{max} = 5$. The magnetic force theorem was applied as described in [25] to calculate inter-atomic exchange interactions as formulated by Liechtenstein [26] and using an extended set of k-points for the Brillouin zone integration. We also calculated the electronic structure and the exchange interaction in the paramagnetic state by modelling it within the disordered local moment (DLM) approximation according to Györffy *et al* [27].

The calculation of the MAE has been done using the relativistic self-consistent electronic structure calculated with moments oriented along the c-axis of the hexagonal unit cell and applying the torque method as described elsewhere [27, 28] with an extended set of the k-points to ensure convergence of the MAE better than 0.01 meV/atom.

3. Results and discussion

Calculated values of the magnetic moments in the ferromagnetic and antiferromagnetic states of MnB_2 are presented in table 1. The results of the KKR-ASA calculations are almost identical to those obtained previously by various authors using other ASA based methods [2, 12, 13]. The magnetic moment in the FM state is much smaller than for the AFM case; however, the latter value is still too small compared to the experimental estimates of 2.6 μ_B/Mn [10]. The FLAPW method correctly predicts the experimental value of the moment for the antiferromagnetic state, whereas the moment obtained for FM is found to be smaller than for AFM, but its value is still much larger then for the ASA calculations. Both methods correctly predict an antiferromagnetic ground state (see table 1). It thus appears that the underestimation of the moment in earlier investigations is merely an artefact of the atomic sphere approximation, rather than being a deficiency of the LSDA or having some other physical reasoning as suggested in [2, 12, 13].

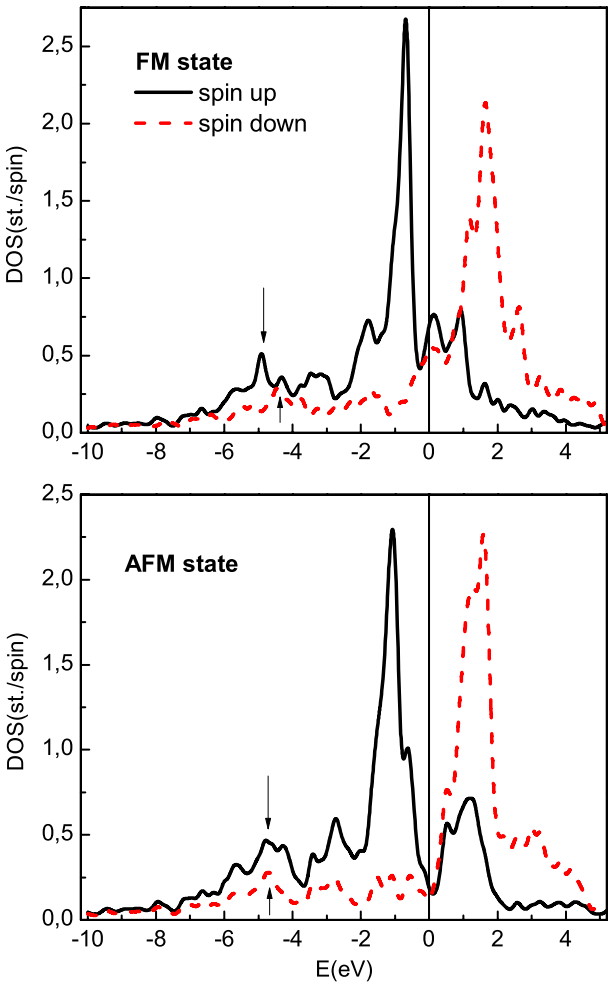

Figure 2. Calculated atom projected density of states of Mn in the ferromagnetic and the layered antiferromagnetic states of MnB_2. Lines represent the spin-up (black) and spin-down (red) DOS. Arrows mark the effects of the covalent magnetism in DOS.

The shortcoming of the ASA calculation is related to the strong covalent bonding between Mn and B and the resulting concentration of charge density in the interstitial region. A careful discussion of this covalency effect can be found in [13]. Here we underline another aspect of the covalency directly related to the magnetism in MnB_2. The strong difference in magnetic moments between the AFM and FM state may point to an itinerant character of the magnetic moments in MnB_2. However, modelling the paramagnetic state above the magnetic ordering temperature within the disordered local moment approximation shows a large local moment value (see table 1) similar to that in the ordered FM state. To help with understanding the difference between FM and AFM states we show in figure 2 the calculated density of states (DOS) for both cases. The positions of the two sharp peaks near the Fermi level which are mainly Mn d states are almost the same in FM and AFM and do not cause any essential difference in the values of in the magnetic moments. The major influence on the values of the moments comes rather from the changes in the spin-up channel from the smaller double peak near the Fermi level. In the AFM

state the Fermi level is in a sort of pseudo-gap of the DOS, whereas for the FM state the DOS at the Fermi level is large. This non-rigid behaviour of the DOS is an example of Kübler's covalent magnetism [1] and is related to the p–d hybridization. The relevance of the B p states to the overall effect can be seen even more clearly in the region well below the Fermi level marked by arrows in figure 2. In this region the predominant contribution to the DOS is provided from the B p states. In particular the non-rigid shift of the related spin-down peak (to ∼0.5 eV), which occurs due to changes in the p–d hybridization, is caused by the different relative orientations of the Mn magnetic moments. We thus conclude (also on the basis of our DLM calculations) that the moments on Mn are well localized and the differences in the moments between the FM and AFM states are mainly due to the effects of covalent magnetism.

The stability of the layered AFM state and the finite temperature magnetic properties can be investigated using the inter-atomic exchange interaction parameters J_{ij} of the classical Heisenberg type Hamiltonian:

$$H = \sum_{ij} J_{ij} \vec{e}_i \vec{e}_j, \tag{1}$$

where $\vec{e}_i$ are the unit vectors of spin at the ith Mn site.

In order to calculate the J_{ij} from first principles we use the Liechtenstein formalism [25] within the KKR method [25]. The three leading nearest neighbour (NN) interactions are presented in table 2, and the most distant interactions are one order of magnitude smaller than the closest one; however, they also cannot be ignored completely for the sake of numerical accuracy of the finite temperature simulation. The pair of atoms connected by these three NN interactions are shown in figure 1. It becomes obvious that the strongest interaction stabilizes the ferromagnetism in the basal planes of Mn atoms. It is interesting that the 2NN interaction between of Mn along the c-axis of the hexagonal structure is also ferromagnetic. The stabilization of the layered AFM structure occurs due to the only slightly smaller 3NN antiferromagnetic interaction between Mn in adjacent planes, which dominates due to the larger number of atoms in the respective neighbour shell. Before we present the results of the Monte Carlo simulations for the Hamiltonian (1) we want to note that the underestimation of the magnetic moment in the KKR-ASA method must lead to some underestimation of the inter-atomic exchange interaction, since these scale approximately as the square of the absolute value of the moment. Indeed the Néel temperature obtained from the Monte Carlo simulation with 14 NN shells is about 15% smaller than the experimental value (see table 2). The value of the Néel temperature from the mean-field approximation is as usual higher than the experimental one and much higher than the MC result. However, our first-principles results for T_N can be regarded as a reasonable estimate and imply that our calculations confirm the local nature of the magnetic moments in the layered antiferromagnet MnB_2, at the same time ruling out any interpretation within weakly itinerant ferromagnetism. The latter may well have occurred due to some foreign phases in single experimental samples. There is of course

Table 2. Calculated exchange constants of an Heisenberg type Hamiltonian (see the text) for first three nearest neighbour shells in MnB_2 (see figure 1). The Néel temperature (T_N) was calculated from the mean-field approximation (MFA) and Monte Carlo simulations (MC). The experimental value ('Exp.') is taken from [11]. The MC simulations were done using exchange constants for ten nearest neighbour shells.

J_{ij} (mRyd)					
1NN	2NN	3NN	MFA T_N (K)	MC T_N (K)	Exp. T_N (K)
1.305	0.142	−0.103	960	640	760

also a correlation between the expected error of KKR-ASA exchange constants and the energy differences between FM and AFM states (table 1) given for the KKR-ASA and FLAPW methods. KKR-ASA underestimates the stability of the AFM state by about 20%, which agrees with the 15% underestimation of T_N from the MC simulation based on the KKR-ASA exchange constants.

Relativistic FLAPW calculations and the application of the torque method [27, 28] allow us to estimate the magnetic anisotropy in MnB_2. We find, in agreement with experiment [10], an easy-plane anisotropy as the Mn moments prefer an orientation within the basal planes. The calculated magnetic anisotropy energy defined as the difference between the energies of the orientation of the moments along the c-direction and within the basal plane is 0.14 meV/Mn. This magnitude is similar to that of the Mn contribution to the total magnetic anisotropy in layered antiferromagnetic materials MnNi (0.17 meV/Mn) and MnPd (0.18 meV/Mn) with tetragonal $L1_0$ structure [19]. However, in the latter materials the second transition element also contributes to the magnetic anisotropy due to a non-trivial spin density distribution induced by the Mn moments, which in some cases even leads to a strong uniaxial anisotropy. In the present case the contribution from the B is negligible, being smaller than the computational accuracy of the present calculation since B is a light p element and any significant spin polarization is absent from the boron sites in the AFM state. The calculated value of the Mn orbital moments is $-0.01\ \mu_B$/Mn, which is again similar to MnNi and MnPd intermetallic values.

4. Conclusions

In this investigation we have demonstrated the local moment character of the magnetism in MnB_2. The stability of the layered antiferromagnetic ground state is unambiguously predicted, and early difficulties concerning the LSDA underestimation of the magnetic moment in this material have been resolved. The first-principles calculations give good estimates for the Néel temperature and correctly predict the type of the magnetic anisotropy. It is also found than the value of the magnetic anisotropy energy in hexagonal MnB_2 is similar to those for cases in which Mn contributes to the total MAE in practical layered Mn based intermetallics. We hope that this work finally resolves the controversial earlier results related to the experimental and theoretical investigation of magnetism in this material.

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