Fundamental Journal of Modern Physics
Vol. 5, Issue 1, 2013, Pages 13-18
Published online at http://www.frdint.com/

ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF $BaMn_2Bi_2$: AB INITIO STUDIES

L. HUA

Department of Physics
School of Information Engineering
Nanjing Normal University Taizhou College
Taizhou 225300, P. R. China
e-mail: pjsd@163.com

Abstract

We have investigated the magnetic properties and electronic structure of $BaMn_2Bi_2$ using density functional theory within the generalized gradient approximation $(GGA) + U$ schemes. We have shown that the ground state magnetic structure of $BaMn_2Bi_2$ is G-type antiferromagnetic. We have suggested that the coupling of Mn 3d with Bi 6p is the source of the G-type antiferromagnetic order.

Introduction

The discovery of high-temperature superconductivity in iron-based arsenide with $ThCr_2Si_2$-type structures [1] has led to finding varieties of physical properties in other 3d-based compounds [2, 7]. In order to understand the cause of high-temperature superconductivity, a number of new 122 classes of non-Fe-based superconductors have been investigated. Additionally, because of the toxic nature of arsenic, chemical substitutions of arsenic with other pnictogens also is another option. Recently, Saparov et al. [8] have reported synthesis of the new 122 ternary

Keywords and phrases: GGA + U, electronic structure, G-type antiferromagnetic, density of states.

Received May 22, 2013; Revised June 4, 2013

transition-metal pnictide of $BaMn_2Bi_2$. They found that $BaMn_2Bi_2$ is crystallized in the body centered tetragonal space group $I4/mmm$ (No.139), $ThCr_2Si_2$-type structure with $a = 4.4902$Å and $c = 14.687$Å. It is antiferromagnetic with anisotropic magnetic susceptibility and semiconducting with a band gap of $E_g = 6$ meV. Heat capacity result confirms the insulating ground state in $BaMn_2Bi_2$. In this paper, we have performed ab initio studies of $BaMn_2Bi_2$ and clarify the internal mechanism of magnetic properties.

Organization of this paper is as follows: In Section 2, the computational method and settings that were used in this study are described briefly. In Section 3, we show theoretical results and discuss the source of the magnetic properties. Finally, we summarize our theoretical findings in Section 4.

2. Computational Method

All calculations were performed using spin-dependent density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) code [9]. The electron-ion interaction was described by the projector-augmented wave (PAW) method [10]. For the XC energy in the generalized-gradient correction, the Perdew-Burke-Ernzerhof (PBE) expression [11] was used. The electronic wave functions were expanded in a basis set of plane waves with a kinetic-energy cutoff of 400 eV. A Γ-centered $5 \times 5 \times 5$ k-point mesh for the Brillouin zone integration was used. The local spin density approximation (LSDA) and GGA are known to fail in the description of the electronic properties of early transition metal (TM) compounds. Thus we have employed the DFT + U [12] methodology which is able to significantly improve predictions of phase stability and magnetic structure. We use here the simple formulation by Liechtenstein et al. [13] and Dudarev et al. [12], where a single parameter U_{eff} determines an orbital-dependent correction to the density-functional theory (DFT) energy. The value of U_{eff} is 2.5 eV in our calculations. 5p6s for Ba, 3d4s for Mn, 6s6p for Bi are treated as valence orbitals in the calculations. Bulk calculations are performed in a $2 \times 1 \times 1$ supercell with 20 atoms. Forces on atoms are calculated and atoms are allowed to relax using a conjugate gradient technique until their residual forces have converged to less than 0.01 eV/Å.

Table 1. The optimized z coordinate for Bi and nearest-neighbor bond distance of $BaMn_2Bi_2$ comparable to the experimental reports

	experiment [8]	This work
z	0.3692	0.3749
d_{Mn-Bi}(Å)	2.8470	2.9003
d_{Bi-Ba}(Å)	3.7109	3.6683
d_{Mn-Mn}(Å)	3.1750	3.1750

3. Results and Discussion

The experimentally measured lattice constant of $BaMn_2Bi_2$ (a = 4.4909Å, c = 14.687Å) was used in our calculations and z coordinate for Bi was optimized.

Table 2. The calculated energy gap E_g(meV), unit molecular energy E(eV) and the average magnetic moment of each atom $\mu(\mu B)$

	experiment	FM	A-AFM	C-AFM	G-AFM
E_g	6	0	0	0	0
DOS	-	1.7	1.46	0.24	0.12
E	-	–26.112	–26.132	–26.456	–26.476
μ_{Ba}	-	0.023	0.000	0.000	0.000
μ_{Mn}	-	4.348	4.349	4.326	4.322
μ_{Bi}	-	0.077	0.057	0.001	0.001

Table 1 lists the optimized z coordinate and nearest-neighbor bond distance of $BaMn_2Bi_2$ and compares with the experimental reports. From Table 1, we can see that our optimized z coordinate and nearest-neighbor bond distance are well consistent with the experimental value. Saparov et al. [8] confirmed the insulating ground state and collinear antiferromagnetic order for $BaMn_2Bi_2$, while the magnetic configuration has not been determined. They suggested that magnetic configuration of $BaMn_2Bi_2$ is likely to be of G-type antiferromagnetic considering the fact that all other $BaMn_2Pn_2$(Pn = P, As, Sb) pnictides order in this magnetic structure. In our ab initio calculation, four types of magnetic configuration are considered. They are collinear ferromagnetic (FM), A-type antiferromagnetic (A-

AFM), C-type antiferromagnetic (C-AFM) and G-type antiferromagnetic (G-AFM). Table 2 lists the calculated energy gap, the total density of states (DOS) at E_f (states eV/$f.u$), unit molecular energy and the average magnetic moment of each atom. From Table 2, the GGA calculated results do not get the band gap. The reason is that the experimental band gap is only 6 meV and GGA results present systematic underestimation of band gap value. The total energy and DOS at E_f decrease from FM to G-AFM. The state of G-AFM has the lowest total energy and density of states at E_f. These results suggest that G-AFM state should be the ground state magnetic configuration of $BaMn_2Bi_2$. Our calculated results are also consistent with the experimental surmise [8]. The calculated magnetic moment of Mn is 4.322 μB which means Mn ions being in the divalent state and in a high-spin configuration. In Figure 1, we show the magnetic interactions between Mn ions in the supercell. Jnn, Jnnn and Jc represent the intralayer nearest neighbor, next nearest neighbor and interlayer nearest neighbor exchange interactions between Mn ions. We adopt the spin Heisenberg model as

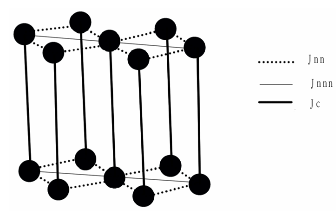

Figure 1. The exchange interactions between Mn ions of $BaMn_2Bi_2$.

$$\hat{H} = -\sum_{i,j} J_{ij}\hat{S}_i \cdot \hat{S}_j.$$

Thus, we get:

$$E_{FM} = E_0 - \frac{10}{4}(16\,Jnn + 12\,Jnnn + 6\,Jc),$$

$$E_{A\text{-}AFM} = E_0 - \frac{10}{4}(16\,Jnn + 12\,Jnnn - 6\,Jc),$$

$$E_{C\text{-}AFM} = E_0 - \frac{10}{4}(\,-16\,Jnn + 4\,Jnnn - 8\,Jnnn + 2\,Jc - 4\,Jc),$$

$$E_{G\text{-}AFM} = E_0 - \frac{10}{4}(\,-16\,Jnn + 6\,Jnnn - 6\,Jnnn - 6\,Jc).$$

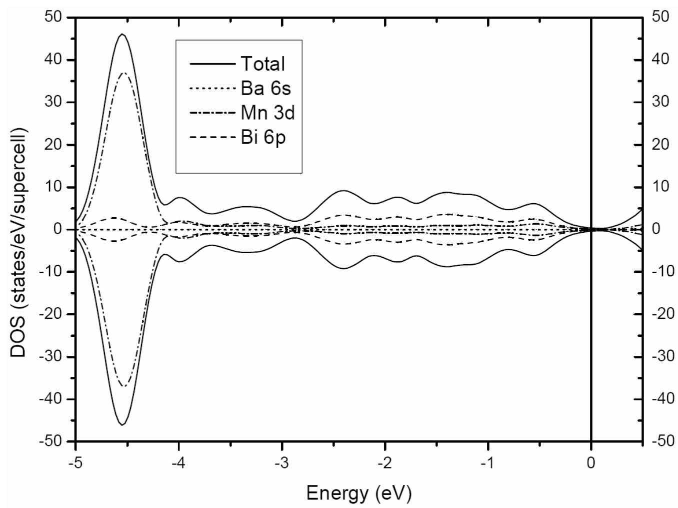

Figure 2. The total and partial density of states (DOS) of Ba 6s, Mn 3d and Bi 6p of $BaMn_2Bi_2$. The energy zero is taken at the Fermi level. The upper halves display the spin-up states and the lower halves the spin-down states.

For this spin Heisenberg model, a positive J corresponds to a ferromagnetic interaction and a negative J to an antiferromagnetic interaction. We use the calculated four kinds of supercell total energy to solve above equations. Thus we get $Jnn = -55.52$ meV, $Jnnn = 78.19$ meV, $Jc = -1.81$ meV. This suggests that the intralayer nearest neighbor exchange interactions between Mn ions are antiferromagnetic and next nearest neighbor ferromagnetic while interlayer exchange interactions of Mn ions are negligible. The results are consistent with our G-AFM calculation. We draw the total density of states (DOS) and partial DOS of Ba 6s, Mn 3d and Bi 6p of $BaMn_2Bi_2$ as shown in Figure 2. We can see that the number of spin up and spin down states are equally, which is consistent with antiferromagnetic ground state. At the Fermi level, the number of states is small and negligible. For Mn 3d state, there is a peak at about -4.5 eV and a strong coupling with Bi 6p from -5 eV to the Fermi level. This kind of coupling suggests that Mn - Bi - Mn superexchange interaction must play an important role in the determination of magnetic structure of $BaMn_2Bi_2$. From real-space analysis, Mn ions are surrounded by four Bi ions which are made of edge-sharing $MnBi_4$ tetrahedra. The d_{xz}, d_{yz} orbitals of Mn 3d hybridize with Bi 6p. The Mn - Bi - Mn bond angles are 66.4° and 101.5°. The superexchange of 66.4°

Mn - Bi - Mn is AFM while 101.5° is FM. This kind of superexchange interaction leads to the G-type antiferromagnetic of $BaMn_2Bi_2$.

4. Summary

In conclusion, we have performed a study of the electronic structure and magnetic properties of $BaMn_2Bi_2$ using first-principles density functional theory within the GGA+U schemes. We have shown that the ground state magnetic structure of $BaMn_2Bi_2$ is G-type antiferromagnetic. By the DOS and real space analysis, we believe that Mn - Bi - Mn superexchange interaction is the main reason for the internal magnetic mechanism.

Acknowledgment

This work is supported by the research projects of Nanjing Normal University Taizhou College (Grant. No. Z201208).

References

[1] M. Rotter, M. Pangerl, M. Tegel and D. Johrendt, Angew. Chem. Int. Ed. 47 (2008), 7949.

[2] D. J. Singh, A. S. Sefat, M. A. McGuire, B. C. Sales, D. Mandrus, L. H. Van Bebber and V. Keppens, Phys. Rev. B 79 (2009), 094429.

[3] Y. Singh, A. Ellern and D. C. Johnston, Phys. Rev. B 79 (2009), 094519.

[4] J. An, A. S. Sefat, D. J. Singh and M. H. Du, Phys. Rev. B 79 (2009), 075120.

[5] B. Saparov and A. S. Sefat, J. Solid State Chem. 191 (2012), 213.

[6] A. S. Sefat, D. J. Singh, R. Jin, M. A. McGuire, B. C. Sales and D. Mandrus, Phys. Rev. B 79 (2009), 024512.

[7] A. S. Sefat, D. J. Singh, R. Jin, M. A. McGuire, B. C. Sales, F. Ronning and D. Mandrus, Physica C 469 (2009), 350.

[8] Bayrammurad Saparov and Athena S. Sefat, J. Solid State Chem. 204 (2013), 32.

[9] G. Kresse and J. Furthmüller, Phys. Rev. B 54 (1996), 11169.

[10] P. E. Blöchl, Phys. Rev. B 50 (1994), 17953.

[11] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77 (1996), 3865.

[12] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Stutton, Phys. Rev. B 57 (1998), 1505.

[13] A. I. Liechtenstein, V. I. Anisimov and J. Zaanen, Phys. Rev. B 52 (1995), R5467.