Study of electronic and magnetic properties of MnS layers

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Self-consistent *ab initio* calculations, based on the density functional theory (DFT) and using the full potential linear augmented plane wave (FLAPW) method, are performed to investigate both electronic and magnetic properties of the MnS layers. Polarized spin and spin–orbit coupling are included in the calculations within the framework of the antiferromagnetic state between two adjacent Mn layers. Magnetic moments considered to lie along axes are computed. Obtained data from *ab initio* calculations are used as input data for the high temperature series expansion (HTSE) calculations to compute other magnetic parameters. The zero-field high temperature static susceptibility series of the spin-4.39 nearest-neighbour Heisenberg model on centred face cubic (FCC) and lattices is thoroughly analysed by a power series coherent anomaly method (CAM). The exchange interactions between the magnetic atoms, the Néel temperature, and the critical exponent associated with the magnetic susceptibility are obtained for the MnS layer.

Keywords: MnS layers, electronic and magnetic structure, magnetic moment, Néel temperature, exchange interactions

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1. Introduction

The diluted magnetic semiconductors (DMSs) have attracted considerable attention both for their important semiconducting properties and for their magnetic properties.[1−4] In DMS, the band electrons and holes strongly interact with the localized magnetic moments and cause a variety of interesting phenomena.[5,6] Manganese sulfide (MnS) is a DMS material (E_g = 3.1 eV) that is of potential interest in short wavelength optoelectronic applications such as in solar selective coatings, solar cells, sensors, photoconductors, and optical mass memories.[7−9] MnS thin films or powders can be found in several polymorphic forms: the rock salt type structure (α–MnS) which is the most common form, by low temperature growing techniques crystallizes into the zincblende (β–MnS) or wurtzite (γ–MnS) structure.[10,11] A large number of experimental and theoretical studies have been carried out for gold and other metallic clusters, mainly due to their involvements in the field of nanoelectronics.[13−15] The magnetic behaviour in atomic clusters also represents an important phenomenon of a reduced dimensionality system, about which little is known. Even though the magnetic cluster at a nanoscale has been of continuous interest, only the advent of new experimental techniques has created an opportunity to fabricate nanostructures with precise structural and chemical qualities, by taking advantage of their different behaviours, compared with their bulk geometry.[16] The effect of sulphur doping on manganese clusters, which is an *ab initio* study, was investigated in Ref. [17].

In the present work two approaches, self-consistent *ab initio* calculation and temperature series expansion (HTSE) calculation, are used to shed light on the magnetic structure. Firstly, the full potential linear augmented plain wave (FLAPW) calculation based on density functional theory (DFT) principle is performed for MnS layers. Appropriate polarized spin and spin–orbit coupling as well as the antiferromagnetic state are considered. Considering the com-

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puted magnetic moment from FLAPW calculations as input data, we use the mean-field theory to find the exchange integrals between the magnetic atoms in the same layer and between the magnetic atoms in the adjacent bilayers. The high temperature series expansions (HTSEs) of the magnetic susceptibility for MnS through two models, Heisenberg and XY, of MnS interacting layers combined with the Padé approximant are studied up to tenth order series in ($\beta = J_{\rm S}/k_{\rm B}T$). The Néel temperature is deduced. The MnS layers used for calculations are shown in Fig. 1.

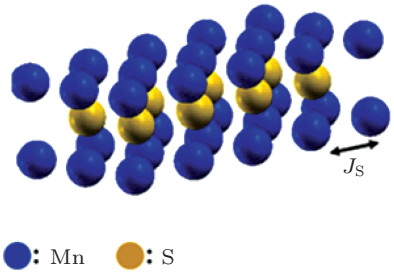


Fig. 1. (colour online) MnS layers used for calculations.

2. *Ab initio* calculations

We use the FLAPW method[18] to perform DFT calculations in the local density approximation with wave functions used as a basis. The Kohn–Sham equation and energy functional are evaluated consistently using the full potential linearized augmented plane wave (FLAPW) method. For this method, the space is divided into the interstitial and the non-overlapping muffin tin spheres centred on the atomic site. The employed basis function inside each atomic sphere is a linear expansion of the radial solution of a spherical potential multiplied by spherical harmonics. In the interstitial region the wave function is taken as an expansion of plane waves and no shape approximation for the potential is introduced in this region which is consistent with the full potential method. The core electrons are described by atomic wave functions which are solved relativistically using the current spherical part; the valence electrons are also treated relativistically in our case. These FLAPW calculations are performed with the crystal structure parameters reported in Ref. [19]. Here, polarized spin, spin–orbit coupling as well as the antiferromagnetic state are considered for Mn adjacent layers. The Mn magnetic moments are considered to lie along a axis.

3. Models and theories

Now, we consider a spin-S Heisenberg model on cubic nets, described by the following well-known Hamiltonian:

$$H = \frac{-J_{\rm S}}{(2m)^2}\sum_{\langle i,j\rangle} S_i S_j - \frac{h}{2m}\sum_i S_i, \qquad (1)$$

where $J_{\rm S}$ is the nearest-neighbour exchange constant, $h = mH_a$, with H_a being the external magnetic field and $m = 4.39\ \mu_{\rm B}$ the magnetic moment per atom. The summation runs over the nearest neighbour pairs. Spin angular momentum operator $2m$ takes a total of $(m+1)$ values — $-2m$, $-2m+1$, …, $2m-1$, $2m$.

We adapt the method of Holland and Brown,[20] to our alloy MnS and we deduce the expression of exchange interaction $J_{\rm S}$ versus Curie Weiss temperature $\theta_{\rm CW}$ as follows:

$$\frac{J_{\rm S}}{k_{\rm B}} = \frac{3}{2m\,(m+2)}[\theta_{\rm CW}], \qquad (2)$$

where $k_{\rm B}$ is the Boltzmann's constant and $m = 4.39\ \mu_{\rm B}$ is the magnetic moment of Mn^{3+} ions, with $\mu_{\rm B}$ being the Bohr magneton. The value of $\theta_{\rm CW}$ is given in Ref. [21].

The high-temperature series of zero-field static susceptibility for the above Heisenberg model can be expressed as

$$\chi(\beta) = \beta\sum_{n=0}^{10} a_n x^n, \qquad (3)$$

with $x = J_{\rm S}/k_{\rm B}T$. The coefficients a_n of MnS layers are given in Table 1 for the Heisenberg model. The coefficient a_n of MnS layers are deduced from those of Heisenberg by using the transformation in Ref. [22]. The obtained results are given in Table 1 for XY model.

Table 1. Series coefficients for the high-temperature developed susceptibility series bcc lattices for MnS layers for Heisenberg and XY model with spin $m = 4.39$.

a_n	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}
Heisenberg	1	1.667	2.6354	4.0841	6.24934	9.48246	14.3032	21.47975	32.14736	47.98263	71.460130
XY	1	3.334	10.541	32.672	99.9894	303.439	915.405	2749.408	8229.725	24567.10	73175.173

4. Results and discussion

4.1. Electronic structure calculations

Total density of states (DOS) of MnS, deduced from band structure calculations, is shown in Fig. 2. Close to Fermi level taken as reference, this DOS is mainly dominated by the contribution of Mn atoms and is not symmetrical with respect to energy axis, pointing to a magnetic moment carried by such atoms. Spin up and spin down from S contributions similarly corroborate that these atoms are, as expected, non-magnetic. The l-decomposed DOSs of

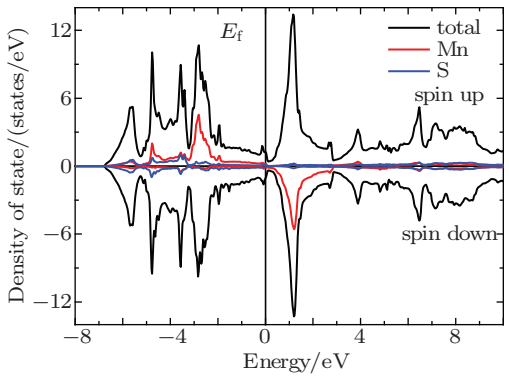


Fig. 2. (colour online) Total DOS and DOSs of Mn and S atoms in MnS layers from FLAPW calculations.

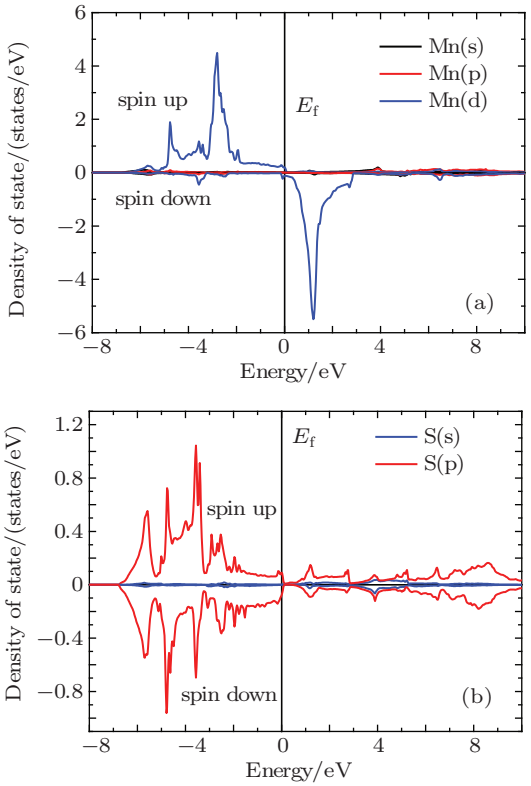


Fig. 3. (colour online) The decomposed DOSs of (a) Mn(s, p, d) and (b) S(s, p) like state in MnS layers from FLAPW calculations.

S(s, p)- and Mn(s, p, d)-like states, shown in Figs. 3(a) and 3(b), provide a more detailed picture and allow us to conclude that the Mn atom has mainly a d character whereas DOS from the S atom is dominated by p-like states. The magnetic moment of Mn is computed as and found to be equal to +4.39 μ_B and −4.39 μ_B in both adjacent layers, respectively. It is noticeable that this estimated magnetic moment value is slightly different compared with 5 μ_B reported in Ref. [23]

4.2. Exchange interaction

We use the magnetic measurement of Curie–Weiss obtained in Ref. [21] to calculate the exchange integrals between the magnetic atoms in the same layer (J_S/k_B) according to the mean-field theory (see Eq. (2)). The obtained value is $J_S/k_B = -8.29$ K.

4.3. Néel temperature T_N

To estimate the Néel temperature T_N for the l-layer, we use the well-known ratio and Padé approximant techniques.[24] Since the ratio plot for a_n/a_{n-1} versus $1/n$ shows oscillatory behaviour, we utilize[25,26] the ratio plot for $(a_n/a_{n-1})^{1/2}$ versus $(1/n\,(n-1))^{1/2}$. The plots of $(a_n/a_{n-1})^{1/2}$ versus $(1/n\,(n-1))^{1/2}$ for n-layer with the free surface are shown in Fig. 4 for the cases of the Heiseneberg and XY model, respectively with spin-4.39.

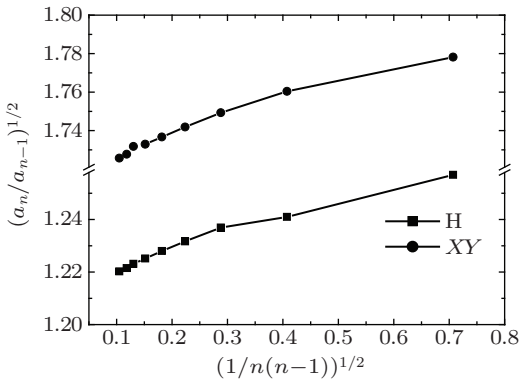


Fig. 4. Ratio plot of the high-temperature developed susceptibility series $(a_n/a_{n-1})^{1/2}$ versus $(1/n(n-1))^{1/2}$ for MnS layer and for Heisenberg and XY models.

In these figures, a straight line can be drawn through the points except those of the lower-order terms. The inverse Néel temperature is estimated from extrapolating the straight line to the asymptotic limit (value of the intercept at $(1/n\,(n-1))^{1/2} = 0$). The obtained values of the Néel temperature for the Heisenberg and XY models are given in Table 2.

Table 2. Critical temperatures of MnS for the Heisenberg and XY models.

Model	Heisenberg	XY
Reduced critical temperature ($x_c = J_S/k_B T$)	1.46	2.92

5. Conclusions

FLAPW calculations are performed to investigate both electronic and magnetic structures for MnS layers. They evidence that the DOS of both Mn and S atoms originates essentially from contributions of 3d and 3p bands, respectively. Magnetic moments carried by Mn atoms are computed and used as input data for HTSE calculations.

The critical properties of spin-4.39 antiferromagnetic Heisenberg and XY models on an MnS centred face cubic structure are investigated by using the high-temperature series expansion of magnetic susceptibility combined with high temperature series expansion. The Néel temperature on the MnS is obtained for the two models. The Néel temperature T_N depends on the studied model ($T_N(XY) > T_N$(Heisenberg)). The obtained values of Néel temperature are comparable to those obtained in Ref. [27] (T_N(Heisenberg) = 1.465 K and $T_N(XY) = 2.39$ K).

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