Electronic structure and magnetic interactions in MnN and Mn₃N₂

Walter R. L. Lambrecht, Margarita Prikhodko, and M. S. Miao

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079, USA

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Electronic structure calculations were performed for MnN and Mn₃N₂ using a full-potential linearized muffin-tin orbital method in the local spin density approximation. Structural relaxation by energy minimization and calculations for various different magnetic configurations were performed. Antiferromagnetic ordering along the [001] direction was found to have the lowest energy in both materials in agreement with experimental neutron diffraction data. The magnetic moments were found to be about 3 µ₂ in good agreement with experiment. Analysis of the partial densities of states reveals that the magnetic moments arise primarily from the t₂g orbitals. In Mn₃N₂, the magnetic moment was found to be slightly larger on the Mn₁ atoms, i.e., the Mn atoms in planes without N than on Mn₂ atoms. Band structures and densities of states are presented. The energy differences between different magnetic configurations were analyzed in terms of a Heisenberg Hamiltonian. We find strong second-nearest-neighbor ferromagnetic interactions for Mn connected collinearly with N, indicative of a double exchange mechanism and about four times weaker nearest-neighbor antiferromagnetic interactions in MnN. In a perfect rocksalt structure, this situation would lead to a multiply degenerate ground state. However, we find that the c/a reduction of about 2% is due to the AFM coupling (it is absent in FM and nonmagnetic MnN) and leads to stronger inter-(001)-plane exchange interactions than intraplane exchange interaction. In Mn₁N₂, the Mn connected via a vacancy lack the strong ferromagnetic interaction. This would suggest a lower Néel temperature for MnN with increasing concentration of N vacancies. However, the nearest-neighbor direct exchange interaction in Mn₁N₂ is found to be about two times as large in Mn₁N₂ than in MnN which partially compensates for the lack of fewer indirect second-nearest exchange interactions. These changes in the exchange interactions are related to the structural relaxations. Nevertheless, the mean field approximation predicts a slightly lower Néel temperature in Mn₁N₂ than in MnN in contrast with experiment. Effects beyond mean field are discussed and are deemed not to be able to provide an explanation for this discrepancy. We suggest that the observed phase transition in Mn₁N₂ previously interpreted as the AFM-paramagnetic phase transition may in reality be an order-disorder transition of the N vacancies.

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I. INTRODUCTION

Mn-N compounds are of interest for a number of reasons. First, there has been recent interest in Mn doping of GaN to develop a dilute ferromagnetic semiconductor with high Curie temperature. However, when the solubility limit of Mn is surpassed, the possibility exists of forming Mn-Ga or Mn-N compound precipitates. Since these may be magnetic on their own, false signatures of dilute magnetic semiconductor behavior may result. MnGa is already well studied and known to be ferromagnetic. However, a better understanding of the magnetic properties of the Mn-N system is required.

Secondly, the Mn-N compounds are already known to exhibit interesting magnetic properties. Several different phases are known in the manganese-nitrogen system. At the Mn-rich end, the e phase is basically an fcc Mn phase with interstitial N and has a nominal composition Mn₂N. At higher N content, there is a hexagonal close packed ζ phase to which belong Mn₂N₂ and Mn₂N. At the other extreme, MnN has a slightly tetragonally distorted rocksalt phase, known as the θ phase. It usually contains a considerable amount of N vacancies and is thus sometimes labeled as Mn₃N₅⁺. Finally Mn₁N₂ corresponds to a ordered vacancy array in MnN and is known as the η phase. In this phase every third (001) layer contains no N at all. The structure can either be described as fct or bct (by rotating the axes 45°). The c/a is further compressed and the Mn and N atomic positions are slightly distorted. The crystal structure is shown in Fig. 1.

In this paper, we will focus on the N-rich end of the phase diagram, i.e., on the η-phase Mn₁N₂ and θ-phase MnN. Recently, thin film growth of MnN and Mn₂N₂ has been reported. Furthermore, the magnetic properties of single crystalline MnN and Mn₁N₂ have been studied by neutron

FIG. 1. (Color online) Crystal structure of Mn₁N₂.
diffraction.\textsuperscript{12,13} Most recently, spin-polarized scanning tunneling microscopy (SP-STM) was carried out on Mn$_3$N$_2$ (010) surfaces.\textsuperscript{14}

The neutron diffraction studies have established both MnN and Mn$_3$N$_2$ to be antiferromagnetic, i.e., with ordering of the magnetic moments along the [001] ordering vector. That is, spins are parallel or ferromagnetically aligned in (001) planes but the direction of magnetization switches direction from one (001) plane to the next. Interestingly, the magnetic moments in MnN were found to be tilted at 23\textdegree{} from the c axis at low temperature and to become parallel to the c axis above 550 K before the magnetization disappears at a Néel temperature $T_N = 660$ K. In Mn$_3$N$_2$, on the other hand, the magnetic moments were found to be directed along the [010]$_{\text{c}}$ direction, i.e. perpendicular to the ordering vector and the Néel temperature in this case was found to be 913-927 K. One problem with this system is that at high temperature the system tends to loose N. The chemical stability as function of temperature was studied by Suzuki \textit{et al.}\textsuperscript{15}

In this paper, we present first-principles electronic structure calculations of MnN and Mn$_3$N$_2$. After briefly describing the computational approach in Sec. II we first present densities of states (Sec. III A) and electronic band structures (Sec. III B) and discuss the origin of the magnetic moments (Sec. III C). Next, we present results for structural relaxation (Sec. III D) and for the energy of different magnetic configurations in Sec. III E. At present only collinear magnetic configurations were studied. Next, we analyze these in terms of a Heisenberg Hamiltonian with effective exchange interactions in Sec. IV. Some interesting aspects of the magnetic interactions of this system are obtained from this analysis. In particular, we find strong second-nearest-neighbor ferromagnetic interactions between Mn coupled via N, indicating the role of double exchange, and weaker first-nearest-neighbor antiferromagnetic interactions, indicating direct exchange. In Mn$_3$N$_2$ second-nearest-neighbor exchange interactions between Mn without intervening N are much smaller. This indicates that N vacancies should tend to lower the Néel temperature, in apparent contrast with the experimental data for $\theta$-MnN and $\eta$-Mn$_3$N$_2$. However, we will show that at the same time the nearest-neighbor exchange interaction is increased, thus compensating at least in part for the reduction in number of second-nearest-neighbor exchanges. Nevertheless, we cannot explain the increase in Néel temperature with increase in N vacancies within a mean field approximation. Effects beyond mean field are considered based on literature studies of the antiferromagnetic Heisenberg and Ising models but cannot explain the discrepancy either. Finally, we will reexamine the experimental evidence for the Néel temperature in Mn$_3$N$_2$ and show that it is incomplete.

\section{II. Computational Methods}

The calculations were carried out within the local density (LDA) and local spin density (LSDA) approximation to the density functional theory\textsuperscript{15} (DFT) using the parametrization of exchange and correlation of von Barth and Hedin\textsuperscript{16} in the spin-polarized case and of Hedin and Lundqvist\textsuperscript{17} in the non-spin-polarized case. A full-potential linear muffin-tin orbital method was employed\textsuperscript{18} which includes calculation of atomic forces and the capability of structural relaxation by a conjugate gradient method. This method uses an optimized basis set consisting of muffin-tin orbitals with smoothed Hankel functions as envelope functions. The smoothing radii and $\kappa$ values (Hankel function decay parameter) were carefully adjusted to optimize an efficient basis set with two $s$, $p$, and $d$ orbitals on Mn and a single $s$, $p$, and $d$ orbital on N. The smooth interstitial quantities are calculated using a fine Fourier transform mesh and the Brillouin zone integrations were carried out with a well converged $k$ mesh based on a division of the reciprocal cell in 10 equal parts in each direction for cubic MnN and equivalent density for the Mn$_3$N$_2$ case and using the tetrahedron method. Except for Sec. III D experimental lattice parameters were used in the calculations.

\section{III. Results}

\subsection{A. Density of states}

First, we show the density of states of idealized rocksalt MnN obtained in a non-spin-polarized calculation in Fig. 2 decomposed in partial densities of states. The cubic lattice constant corresponding to the same volume per atom as in the experimental structure of MnN is adopted in these calculations. In the energy region displayed we see the N 2$p$ with Mn 3$d$ bonding and antibonding states below and above the Fermi level, respectively, and two sharp peaks corresponding to Mn 3$d$ essentially nonbonding or weakly $\pi$-bonding and antibonding states close to the Fermi energy. The latter correspond to the $t_{2g}$ orbitals $d_{xy}$, $d_{yz}$, and $d_{xz}$, while the bonding and antibonding states involve the $e_g$ states $d_{3z^2-r^2}$ and $d_{x^2-y^2}$. One may note that the Fermi level falls right on the first high peak of the density of states, indicating that the Stoner criterion for magnetism is likely to be fulfilled and the development of a magnetic moment may stabilize the system.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{(Color online) Density of states of rocksalt Mn without spin polarization and its decomposition in partial contributions and cumulative integral assuming experimental volume per atom.}
\label{fig2}
\end{figure}
Next, we show the density of states of ferromagnetic MnN and its decomposition in terms of \( \text{Mn} t_{2g} \), \( \text{Mn} e_g \), and \( \text{N} p \) states in Fig. 3. Spin up and spin down are displayed with different signs as usual and the cumulative integrals over this curves are also shown and allow one to analyze the contribution of each type of orbital to the magnetic moment. We now see that the minority spin \( t_{2g} \) bands are pushed above the Fermi level while the majority \( t_{2g} \) bands lie entirely below the Fermi level. The \( e_g \) bands have both spin up and spin-down contributions to the bonding states with \( N \) below the Fermi level.

A similar conclusion holds for the antiferromagnetic case shown in Fig. 4. In this case, we use both the experimental lattice parameters \( a \) and \( c/a \). The only difference is that now the spin-up DOS on one Mn, equals the spin-down DOS on the other Mn. Only one of the two Mn atoms is shown.

Moving on to \( \text{Mn}_3\text{N}_2 \), shown in Fig. 5 for the ferromagnetic and Fig. 6 for the antiferromagnetic case, respectively, we see considerable change in the DOS compared to MnN. Here, we used the lattice parameters \( c/a \) and internal parameters as calculated in Sec. III D, except that the overall length scale or volume per atom was taken from experiment to avoid the LDA underestimate. In particular, we note a much broader and fine-structured band between the Fermi level and \(-4\) eV. Also this energy range now contains significantly stronger \( e_g \) contributions. This is an indication of the fact that the distortions from the perfect octahedral environ-
ment, to be discussed in more detail later, lead to a mixing of \( e_g \) and \( t_{2g} \) states. For example, the \( \text{Mn}^{2+} \) \( e_g \) peaks at \(-1.6\) and \(-1.2\) eV in the AFM case in fact arise predominantly from the \( d_{x^2-y^2} \) contribution. In the FM case, we showed the \( \text{Mn}^{1+} \) contributions times a factor two because there are two equivalent \( \text{Mn}^{1+} \) and the \( \text{Mn}^{2+} \) times a factor 4 because there are four equivalent \( \text{Mn}^{2+} \) in the cell. For the AFM case, the \( \text{Mn}^{1+} \) PDOS on one of the \( \text{Mn}^{1+} \) equals the \( \text{Mn}^{1+} \) PDOS on the other \( \text{Mn}^{1+} \) and similar for \( \text{Mn}^{2+} \). We thus show the PDOS multiplied respectively by a factor 1 and 2 for \( \text{Mn}^{1+} \) and \( \text{Mn}^{2+} \).

B. Band structure

The band structure along the high symmetry axes of the Brillouin zone are shown in Figs. 7, 8, and 9 for \( \text{MnN} \) in the non-spin-polarized ferromagnetic and antiferromagnetic cases, respectively. All of these were calculated at experimental lattice parameters as in the previous section. One can see that the \( \text{Mn} \) 3\( d \) and \( \text{N} \) 2\( p \) bands form a strongly hybridized manifold of states. The \( \text{N} \) 2\( s \) bands form the lower band. At \( \Gamma \), one may note two threefold degenerate states close to each other followed by a twofold degenerate level, corresponding to the \( \text{N} \) 2\( p \) and \( \text{Mn} \) 3\( d \) 2\( g \) and \( \text{Mn} \) \( e_g \) states, respectively. In the nonmagnetic case, one may notice that over a large part of the Brillouin zone, e.g., along \( X-W-L \), the bands are rather flat close to the Fermi level and lead to the high density of states seen in the previous section. In the ferromagnetic case, these bands are spin split and moved away from the Fermi level. For the AFM case, the bands become folded in the smaller \( BZ \) corresponding to the body-centered tetragonal unit cell. We show the bands only along the \( x \) and \( z \) directions.

The basic energy level scheme can be summarized in the schematic Fig. 10. Since in \( \text{MnN} \) \( \text{Mn} \) is trivalent, we are concerned with a \( d^4 \) configuration. The \( t_{2g} \) levels of up and down spin straddle the Fermi level. These essentially non-bonding states take 3 of the 4 electrons in the majority spin state and contribute 3\( \mu_B \) to the magnetic moment. The \( e_g \) levels form bonding and antibonding states with \( \text{N} \) \( p \) of which the antibonding states of the minority spin remain unfilled while the bonding states have both majority and minority spin character. The remaining \( d \) electron is spread over these states. One thus concludes that the magnetic moment should be slightly above 3 and less than 4.

C. Magnetic moments

The calculated magnetic moments in \( \text{MnN} \) and \( \text{Mn}_3\text{N}_2 \) are given in Table I and compared with the results from
TABLE I. Magnetic moments in MnN and Mn$_3$N$_2$ calculated at experimental volume per atom. (all values in $\mu_B$).

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<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Experiment</th>
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<tr>
<td></td>
<td>FM</td>
<td>AFM</td>
</tr>
<tr>
<td>$t_{2g}$</td>
<td>2.30</td>
<td>2.36</td>
</tr>
<tr>
<td>$e_g$</td>
<td>0.85</td>
<td>0.94</td>
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<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Experiment</th>
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<tr>
<td></td>
<td></td>
<td>Mn$_3$N$_2$</td>
</tr>
<tr>
<td>$t_{2g}$</td>
<td>1.26</td>
<td>1.65</td>
</tr>
<tr>
<td>$e_g$</td>
<td>0.94</td>
<td>1.15</td>
</tr>
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</table>

First, we note that the magnetic moment in the nearly touching muffin-tin radii do not exactly add up to the total magnetic moment per unit cell in the ferromagnetic case. We thus renormalize the magnetic moments per atom to the total magnetic moment and apply the same renormalization factor for the AFM case. We note that both for MnN and Mn$_3$N$_2$, the calculated magnetic moments are slightly larger for the AFM than for the FM alignment of the spins. This may contribute to the fact that the AFM phase has lower energy, although a more appropriate discussion of the magnetic energy differences in terms of exchange interactions will be presented in Sec. IV. Secondly, we note that in Mn$_3$N$_2$ the magnetic moment is slightly larger on the Mn$_1$ atom, i.e., the Mn lying in the plane without any N than on the other Mn. The experimental neutron diffraction data were unable to decide this point since either one of the two sets of values provided an equally good fit to the data. The only conclusion one could safely draw from the neutron diffraction data and in agreement with our calculations is that the magnetic moment on both atoms differ only by a small amount. Our calculated magnetic moment for the AFM MnN is in excellent agreement with the experimental data while for Mn$_3$N$_2$ they appear somewhat underestimated. An underestimate is actually expected for the LSDA and the almost perfect agreement for pure MnN is therefore somewhat fortuitous. In fact, the $\theta$-phase materials in the experiment, designated here as MnN, corresponded rather to Mn$_{0.52}$N$_{5.26}$ or Mn$_{0.88}$N$_{0.12}$, in other words, it contained a significant number of N vacancies.

As already discussed above, the magnetic moments originate primarily from the $t_{2g}$ orbitals. Further detail on the decomposition of the magnetic moments into their $t_{2g}$ and $e_g$ contributions is provided in Table I.

We find that the magnetic moments decrease with decreasing lattice constant, as shown in Fig. 11 for FM MnN.

### D. Structural relaxation

Our structural relaxation results are summarized in Table II. For MnN we optimized the $c/a$ ratio and calculated the energy as function of lattice constant in the nonmagnetic, FM and AFM configurations. For both the nonmagnetic and FM cases, the $c/a = 1$, indicating a perfect rocksalt structure. For the AFM case, we find the $c/a$ ratio to be 0.978, in excellent agreement with experiment, as shown in Fig. 12. The fact that the $c/a$ distortion only occurs for the AFM configuration indicates that it is magnetic in origin. In other words, there is a magnetic strain effect.

The energy as function of the $a$ lattice constant is shown in Fig. 13 for the nonmagnetic, FM and AFM cases. The $a$ lattice constant represents the absolute length scale of the system and is significantly underestimated by the LSDA, namely, by 5.2 and 4.7 % for the FM and AFM cases, and even worse, by 6.8% in the nonmagnetic LDA case. This amounts to an underestimate of the equilibrium volume of the order of 15%. From the curvature of the energy as function of lattice constant for the AFM case, we deduce a bulk modulus $B = 262$ GPa. The cohesive energy (neglecting zero point motion) is 11.4 eV/MnN unit.

We note that the energy difference between the nonmagnetic state and the FM and AFM states is considerably larger.

### TABLE II. Structural relaxation results for AFM MnN and Mn$_3$N$_2$

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<th>Theory</th>
<th>Experiment</th>
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<tr>
<td></td>
<td>MnN</td>
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<tr>
<td>$a$ (Å)</td>
<td>4.086</td>
<td>2.825</td>
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<tr>
<td>$c/a$</td>
<td>0.978</td>
<td>4.077</td>
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<tr>
<td>$E_{coh}$ (eV)</td>
<td>11.4</td>
<td>262</td>
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<tr>
<td>$d_{1}$ (c)</td>
<td>0.178</td>
<td>0.167</td>
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<tr>
<td>$d_{2}$ (c)</td>
<td>0.159</td>
<td>0.159</td>
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than the difference between FM and AFM states. Furthermore, we find that as the lattice constant decreases, the energy difference between FM and AFM configurations decreases, indicating a possible lowering of the Néel temperature with pressure. At some point the two curves cross. In fact, near the calculated equilibrium lattice constant of the magnetic configurations, the energy difference between AFM and FM is almost negligible and the FM minimum energy is slightly $\approx 2$ meV lower than that of the AFM minimum. A ferromagnetic groundstate is in disagreement with experiment and is probably due to the serious underestimate of the lattice constant by LSDA. We thus used the experimental lattice constant rather than our calculated equilibrium lattice constant in all but this section of the paper. It does indicate though that the magnetic properties are sensitive to the lattice volume and that compression may favor a ferromagnetic configuration.

For Mn$_3$N$_2$, there are two intracellular degrees of freedom to relax besides the $c/a$ ratio and the lattice constant. These correspond to the vertical distance (along [001]) between the Mn$_1$ and the Mn$_2$, $d_1$, and the Mn$_1$-N distance $d_2$.

![Figure 12](image1.png)

**FIG. 12.** Energy of AFM MnN per MnN unit as function of $c/a$.

![Figure 13](image2.png)

**FIG. 13.** Energy per MnN unit as function of lattice constant for different magnetic configurations.

In Table III we compare the energies for different magnetic configurations for both MnN and Mn$_3$N$_2$. All of these are calculated at the experimental volume per atom. They are all given relative to that of the FM case, which itself is found to be 0.68 eV lower in energy than the nonmagnetic case for MnN. First, we note that the experimentally observed ordering AFM-I or ordering along [001]$_1$ with period 1 is indeed

<table>
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<th>MnN</th>
<th>Mn$_3$N$_2$</th>
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<tr>
<td>[001]$_1$</td>
<td>↑↑↑↑↑</td>
<td>↑↑↑↑↑</td>
</tr>
<tr>
<td>[111]$_1$</td>
<td>↑↑↑↑↑</td>
<td>218</td>
</tr>
<tr>
<td>[100]$_1$</td>
<td>↑↑↑↑↑</td>
<td>-46</td>
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<tr>
<td>[001]$_2$</td>
<td>↑↑↓↓↓</td>
<td>34</td>
</tr>
<tr>
<td>[001]$_3$</td>
<td>↑↑↓↓↓</td>
<td>18</td>
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<tr>
<td>[001]$_{1,2}$</td>
<td>↑↑↑↑↓</td>
<td>3</td>
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<tr>
<td>[001]$_{2,1}$</td>
<td>↑↑↑↑↑</td>
<td>3</td>
</tr>
<tr>
<td>[001]$_{2,4}$</td>
<td>↑↑↑↑↑</td>
<td>21</td>
</tr>
<tr>
<td>[001]$_{3,2}$</td>
<td>↑↑↑↑↓</td>
<td>21</td>
</tr>
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</table>

which are indicated in Fig. 1. Note that Mn$_1$ is the Mn in the plane with N vacancies and Mn$_2$ is the other Mn in planes with N. Ideally this distances correspond to $1/6 = 0.167$ of the $c$ lattice constant. We see that the distortion can be interpreted as an outward puckering of the N from the Mn-N double layer and a contraction of the Mn-Mn distance within the Mn-N double layer. This is similar to the expected relaxation of an ionic rocksalt structure at the $001$ surface where the anions move outward. One may thus interpret the structure as a superlattice of a pure Mn monolayer with a MnN double layer rocksalt structure. The ideal value of the $c/a$ ratio is $6\sqrt{2} = 4.242$. The actual value of $c/a$ is found to be 4% smaller, indicating a stronger $c/a$ reduction than in pure MnN where the $c/a$ reduction is only 2%. This is of course related to the abovementioned contraction of the Mn-N double layer. Again the lattice constant $a$ is underestimated by about 5%. We note that the $a_{cst} = a_{cst} \sqrt{2}$ which is 3.995 Å theoretically and 4.205 Å experimentally. This indicates a contraction of the lattice constant compared to MnN also occurs in plane. Both the in-plane and perpendicular to the plane contractions compared to MnN indicate an increase in direct Mn-Mn bonding.

The underestimate of the lattice constant or overbinding by LDA is well known and is more severe in transition metals and their compounds. The magnetic moments in the previous section were therefore calculated at the experimental lattice constant rather than at our calculated minimum energy lattice constant. Both the lattice constant and magnetic moment underestimates probably find their origin in the inadequate treatment of the LSDA for fairly narrow $d$-band systems. LSDA underestimates correlation effects and the trend toward magnetism.

### E. Magnetic energies

In Table III we compare the energies for different magnetic configurations for both MnN and Mn$_3$N$_2$. All of these are calculated at the experimental volume per atom. They are all given relative to that of the FM case, which itself is found to be 0.68 eV lower in energy than the nonmagnetic case for MnN. First, we note that the experimentally observed ordering AFM-I or ordering along [001]$_1$ with period 1 is indeed
found to have the lowest energy for both systems. Furthermore, this configuration is found to be further below the ferromagnetic energy for Mn$_3$N$_2$, indicating a larger stabilization of AFM order. This might in a rough approximation be viewed as being consistent with a larger Néel temperature in Mn$_3$N$_2$, but we will show in the Sec. IV that this is not correct in view of second-nearest-neighbor interactions.

Secondly, we note that the other commonly occurring AFM ordering AFM-II or ordering along the [111] direction is in fact higher in energy than the FM state. The consequences of this will be discussed in the next section. It indicates ferromagnetic interactions between second-nearest neighbors dominate antiferromagnetic interactions between nearest neighbors.

We also find that an alternative magnetic configuration with a repeat period of three layers [001]$_3$ has higher energy than the configuration in which the spin flips every layer. This configuration might have appeared plausible in Mn$_3$N$_2$ in view of the chemical periodicity consisting of two layers of MnN and one layer of pure Mn. However, it can clearly be ruled out. The other configurations were studied in an attempt to obtain a deeper insight in the magnetic exchange interactions and will be discussed in the next section.

IV. DISCUSSION

A. Heisenberg model

In this section, we discuss the magnetic interaction energies in terms of a Heisenberg Hamiltonian

$$H = - \sum_{\langle mn \rangle} J_{mn} S_m \cdot S_n,$$

(1)

where the sum is over all pairs of sites in the lattice. The general idea is to evaluate the energy of a given magnetic configuration while making certain simplifying assumptions on the $J_{mn}$ to include and map it to the corresponding energy calculated from first-principles. For instance, we may assume only nearest-neighbor interactions or only first- and second-nearest-neighbor interactions. Refinements might be to distinguish intralayer and interlayer interactions (in view of the $c/a$ distortion), or to include different next-nearest-neighbor interactions between Mn if they have N in between them or not. Clearly, we need to study the convergence of the interactions in the model. The procedure is known in alloy theory as the Connolly-Williams procedure.$^{19}$ We map the energy of a given model to the first-principles results and then apply these to other configurations not in the original set as a test of convergence of the model. Finally, we can apply them to the statistical mechanics problem of how the spin system behaves as function of temperature. Since the Heisenberg Hamiltonian here is supposed to describe the angular dependence of the spin interactions, we map the energy of the model to the difference in energy between a given magnetic configuration and ferromagnetic alignment. This does not include the energy involved in producing the magnetic moments in the first place. The idea is that the magnetic moments stay fixed in size from sphere to sphere but have different orientations. The decoupling of these two degrees of freedom is well justified in the so-called rigid spin approximation.$^{20}$ As we have seen in Sec. III C the magnetic moments are slightly larger in the AFM than in the FM configuration and thus we cannot strictly say that the magnetic energy differences will result purely from the orientation of the magnetic moments, but we will for simplicity ignore this complication in this section.

Within a mean-field theory the Néel temperature is given by

$$T_N = \frac{1}{3k} \left( \sum_{n \in A} J_{mn} - \sum_{n \in B} J_{mn} \right),$$

(2)

for spin $m \in A$ and where $A$ an $B$ are the two sublattices on which a different macroscopic magnetization occurs below the Néel temperature. While a mean field approximation typically overestimates the actual critical temperature, the degree of error produced by it depends from system to system. We will return to this question at the end of this section. Next, we discuss various levels of approximination of this general idea.

B. Second nearest-neighbor model

If we include first and second-nearest-neighbor interactions between Mn, we obtain the following energies for MnN magnetic configurations:

$$E_{AFM-I} = 2 J_1 - 3 J_2,$$

$$E_{AFM-II} = 3 J_2,$$

$$E_{FM} = -6 J_1 - 3 J_2.$$  

(3)

Mapping these to the first-principles results for MnN, we obtain

$$J_1 \approx -9 \text{ meV}, \quad J_2 \approx 45 \text{ meV},$$

(4)

indicating that second-nearest-neighbor interactions are ferromagnetic and about five times larger than the antiferromagnetic nearest-neighbor interactions. It is well known that for three atoms in a collinear configuration the double exchange mechanism can provide a strong ferromagnetic coupling. This coupling arises from the $e_g$ orbitals which point directly toward the N 2p orbitals. As we discussed in Sec. III B there is essentially only one $e_g$ electron per Mn and thus, the Anderson-Hasegawa model$^{21}$ indeed predicts ferromagnetic double exchange rather than antiferromagnetic super exchange.

Interestingly, if we consider what the ground state is of the Heisenberg Hamiltonian with these interactions, we find that there is strong frustration in the system. For example, a configuration in which the spins on the four fcc sublattices are pointing at 109.47° from each other, i.e., in the directions of a regular tetrahedron, and hence, $S_i \cdot S_j = -1/3$ for $i$ and $j$ in different sublattices, has as energy, $-2 \cdot 3 \cdot J_1 \cdot (-1/3) - 3 J_2$, exactly the same energy as the AFM-I configuration. This indicates an inability for the system to decide in which direction to break the symmetry.$^{22}$
However, if we take into account that interactions $J_{1,1}$ between different (001) layers could be slightly stronger than those in a (001) plane ($J_{1,1}$), we find that the AFM-I configuration would have lower energy. In fact, the above non-colinear arrangement of the spins then has energy $2(J_{1}) + 2J_{1,1}/3 - 3J_{2}$ while the AFM-I energy is $-2J_{1} + 4J_{1,1} - 3J_{2}$. To test this further we have calculated the [100]$_{1}$ AFM configuration while still maintaining the $c/a$ ratio equal to 0.98. We find that $J_{1} = -6$ meV, slightly smaller than $J_{1} = -9$ meV. This indicates that the actual reduction of the $c/a$ ratio from 1 in this system is related to stabilizing a specific magnetic order. In other words, there is a magnetoelastic coupling or magnetically generated strain in the system, as we already mentioned in Sec. III D.

Considering that the strongest magnetic interaction now appears to be a ferromagnetic double exchange interaction between Mn coupled by a collinear N in between, it becomes of interest what happens if we introduce vacancies in the system as in Mn$_3$N$_2$. Intuitively, one would expect that the second nearest neighbor interaction between Mn without intervening N would be much smaller and possibly even zero. In that case, it is clear that the more N vacancies we have in the system, the fewer terms will contribute to the second term in Eq. (2) and hence the prediction would be that the Néel temperature would decrease with increase of the N vacancies. This is contrary to the experimental observations. Clearly then if we have fewer second-nearest-neighbor interactions, the remaining ones must become stronger if we want to explain the higher Néel temperature for systems with less N.

C. Longer range interactions in MnN

In order to obtain a clearer comparison between the exchange interactions in MnN and Mn$_3$N$_2$, and to test the convergence of the Heisenberg Hamiltonian considered, we decide to study the same spin configurations in both materials. We picked basically various arrangements of the spins all along the [001] ordering vector but with different periodicity.

We first discuss MnN. Since the spins in the (001) planes in all these configurations are ferromagnetically aligned and are always the same, only interactions between layers appear in the energy differences and the problem thus maps on the well-known one-dimensional anisotropic next-nearest-neighbor Ising (ANNNI) model which is used to describe the polytypism in SiC. If we call the ANNNI model parameters $I_{1}$, $I_{2}$, $I_{3}$, the mapping to the pair interactions $J_{p}$ is $I_{1} = 4J_{1}$, $I_{2} = 2J_{2} + 4J_{1}$, and $I_{3} = 4J_{3}$, where in fact these are all $J_{p}$ if we wish to distinguish them from in-plane $J_{||}$ interactions.

The energy differences from the FM state of the various magnetic configurations considered in Table III can be expressed in terms of the $I_{n}$ as follows:

$$\Delta E([001]) = \frac{2}{3}I_{1} + \frac{4}{3}I_{2} + 2I_{3},$$

$$\Delta E([001]_{1,2}) = I_{1} + 2I_{2} + I_{3},$$

$$\Delta E([001]_{1,2}) = \frac{4}{3}I_{1} + \frac{4}{3}I_{2},$$

$$\Delta E([001]_{2,3}) = \frac{2}{3}I_{1} + \frac{4}{3}I_{2} + \frac{4}{3}I_{3}. \quad (5)$$

We note that $2\Delta E([001]_{1,2}) - \Delta E([001]) = 4I_{2}$ and $\Delta E([001]_{1,2}) - \Delta E([001]_{1}) = \frac{2}{3}I_{2}$. This fixes $I_{2}$ = 34.25 meV and $I_{3}$ = -4.5 meV. We then obtain $I_{1}$ = -30 meV from the first of Eqs. (5) or $J_{1}$ = -7.5 meV. This model fits all the equations pretty well, giving -69, 34, 17, 6, 20 meV, respectively. Since $I_{3}$ = 4$J_{5}$ it shows that $J_{5}$ = -1 meV is almost negligible. If we also assume $J_{3}$ and $J_{4}$ to be negligibly small compared to the dominant $J_{2}$, we are reduced back to a model with only two pair interactions. However, since the energy differences of these configurations all corresponding to different stackings along the [001] directions were obtained more accurately from the first-principles calculations by using equivalent size unit cells or equivalent k-point sets, it is more advisable to obtain $J_{1}$ and $J_{2}$ from these energy differences than from the AFM-I and AFM-II configurations as done in the previous section. Using only the $\Delta E([001])$ and $\Delta E([001]_{1,2})$, we obtain a new estimate of $J_{1}$ and $J_{2}$ as follows:

$$J_{1} \approx -9 \text{ meV}, \quad J_{2} \approx 34 \text{ meV}, \quad (6)$$

showing that the ratio of $J_{2}/J_{1} \approx -4$. This gives, -72, 32, 21, -3, and 21 for the configurations of Eq. (5) and 204 meV for AFM-II, in excellent agreement with the first-principles results of Table III.

D. Convergence of model for Mn$_3$N$_2$

Next, we turn back to Mn$_3$N$_2$. We now need to distinguish $J_{2}$ for Mn connected by N from $J_{2}$ for Mn connected by a N vacancy. We first consider the [001]$_{1,2}$ and [001]$_{2,1}$ configurations. In the MnN case, these are obviously the same whereas in the Mn$_3$N$_2$ case, they differ because the spin flip occurs between the two Mn$_3$ layers in the last one and in between the Mn$_1$ and Mn$_2$ in the former case. We obtain

$$E([001]_{1,2}) - E([001]_{2,1}) = \frac{2}{3}(J_{2} - J_{2}'), \quad (7)$$

showing that this energy difference will give us the difference between $J_{2}$ and $J_{2}'$. More completely, we obtain the following for the energy differences from the FM configuration

$$\Delta E([001]) = 8J_{1},$$

$$\Delta E([001]_{3}) = \frac{8}{3}J_{1} + \frac{2}{3}J_{2} + \frac{2}{3}J_{2}'. \quad (8)$$
Thus, from the first two of these we can obtain $J_{MnN}$, whereas in $Mn_{3}N_{2}$, the $J_{Mn2}$ introduction of vacancies has been compensated by an increase of $J_{1}$.

E. Comparison of $MnN$ and $Mn_{3}N_{2}$ exchange parameters

Having obtained a satisfactory Heisenberg model with just first and second-nearest-neighbor interactions, we may now compare the results for $MnN$ and $Mn_{3}N_{2}$. Clearly, $J_{2}$ has not changed much but $J_{1}$ has increased by about a factor two. Thus, the reduced number of FM interactions by the introduction of vacancies has been compensated by an increased nearest-neighbor AFM interaction. Comparing the Mn-Mn distances, we find 2.979 Å in $MnN$, whereas in $Mn_{3}N_{2}$, the $Mn_{2}−Mn_{2}$ distance is 2.733 Å and the $Mn_{1}−Mn_{2}$ distance is 3.016 Å. Clearly the average Mn-Mn distance between layers, which are the only ones involved in the energy differences of magnetic configurations considered, is decreased to 2.875 Å, i.e., by 4% from that in $MnN$. This is in part due to an overall smaller lattice constant $a_{bc}$ and in part due to the structural distortion. The increase of the $Mn_{1}−Mn_{2}$ distance is only by 1% and the decrease of the $Mn_{2}−Mn_{3}$ distance is by 8%. This suggests introducing different $J_{1,2}^{1−2}$ and $J_{1,2}^{2−3}$ for interlayer exchanges between $Mn_{1}−Mn_{2}$ and $Mn_{2}−Mn_{3}$, respectively. This would change the expressions terms involving $J_{1}$ in Eqs. (8) as follows:

$$8J_{1} \rightarrow \frac{8}{3}(2J_{1}^{1−2}+J_{1}^{2−3}),$$

Assuming the $J_{2}$ and $J_{2}'$ stay as before, one can try to extract a difference between $J_{1}^{1−2}$ and $J_{1}^{2−3}$ from this but we find that the two differ by less than 1 meV, with $J_{1}^{1−2}$ being slightly larger than $J_{1}^{2−3}$. Thus, this complication of the model seems unnecessary. Overall, however, we can expect that the shorter Mn-Mn distance and the fact that Mn lacks some of the N to bond to leads to a stronger direct Mn-Mn bonding in $Mn_{3}N_{2}$. A stronger overlap of Mn wave functions will tend to strengthen their direct antiferromagnetic exchange. From this point of view, it is slightly surprising that for $MnN$ as function of volume we found a decrease in $E_{FM}−E_{AFM}$ with decreasing lattice constant in Sec. III D. This indicates that it is perhaps not as much the distance changes as the rehybridizations that play a role. We expect the $e_{g}$ orbitals to be primarily involved with N p and leading to the indirect ferromagnetic second-nearest exchanges. The nearest-neighbor direct exchanges are primarily due to the Mn $t_{2g}$ orbitals. Indications of rehybridization and mixing up of these orbitals were pointed out in our analysis of the partial densities of states.

F. Néel temperatures

Having established the basic convergence of the Heisenberg model, we turn our attention now to the Néel temperatures. Including $J_{1}$ and $J_{2}$, but counting $J_{2}$ only when Mn is coupled via N, we obtain in mean field approximation from Eq. (2).

$$T_{N}(MnN)=(-4J_{1}+4J_{2})/3k,$$

$$T_{N}(Mn_{3}N_{2})=(-4J_{1}+6J_{2})/3k,$$

which gives 928 K for $MnN$ and 820 K for $Mn_{3}N_{2}$. Thus, we obtain a lower Néel temperature for $Mn_{3}N_{2}$ in contradiction with experiment. We next examine various possible explanations for this. First, we consider effects beyond the mean field approximation.

G. Beyond mean field

The mean field approximation for antiferromagnetic systems is known to deviate rather strongly from Monte Carlo simulations. For the fcc Heisenberg antiferromagnet with
model with second-nearest-neighbor interactions would give but it seems unlikely that this will resolve the discrepancy.

H. Experimental evidence

Next, we reconsider the experimental results. Leineweber et al.\textsuperscript{13} observed that the magnetic susceptibility of \( \eta = \text{Mn}_3\text{N}_2 \) behaved essentially as a Pauli paramagnet at ambient temperatures and obtained their first estimate of the Néel temperature from a maximum of the susceptibility at about 913–923 K. Differential scanning calorimetry (DSC) measurements showed a signature of a phase transition at 927 K upon heating and 916 K upon cooling. This was interpreted as an antiferromagnetic-paramagnetic phase transition. For MnN, both DSC and temperature dependent neutron diffraction determined the phase transition temperature to be 660 K. These authors, however, also noted that the enthalpy discontinuity of the phase transition is significantly larger for \( \text{Mn}_3\text{N}_2 \) than for MnN and speculated that in \( \text{Mn}_3\text{N}_2 \), there may be a contribution of \( \text{N} \) disordering at the transition temperature. On the other hand, we note that according to the Monte Carlo studies of Phani et al.\textsuperscript{25} the transitions for ratios of the parameters \( \alpha > 0.25 \) are probably second order and show no clear discontinuity even for the largest samples considered. This suggests that perhaps, the actual AFM-paramagnetic phase transition in \( \text{Mn}_3\text{N}_2 \) was missed and the transition observed at about 925 K may be entirely an order-disorder transition of the \( \text{N} \) vacancies. No direct evidence of the magnetic nature of this transition is available. This should not be too surprising considering that there is actually evidence of loss of \( \text{N} \) at high temperature in these materials.\textsuperscript{10,13} Thus one may well expect \( \text{N} \) to become mobile and a disordering of the \( \text{N} \) vacancies is expected. We conclude that further experimental study of the neutron diffraction as a function of temperature in \( \text{Mn}_3\text{N}_2 \) would be of considerable interest.

V. CONCLUSION

In conclusion, we have obtained the basic electronic structure and magnetic properties of MnN and \( \text{Mn}_3\text{N}_2 \) using standard first-principles collinear local spin-density functional calculations. The magnetic moments can be easily understood in terms of the partial densities of states and the basic energy level scheme and band filling. We obtained good agreement with the experimental finding of antiferromagnetic ordering along the [001] direction, so-called AFM-I for both MnN and \( \text{Mn}_3\text{N}_2 \). Our analysis of the total energies of different spin configurations revealed that this system is characterized by strong second-neighbor Mn-Mn interactions due to the double exchange mechanism via N while the nearest-neighbor interactions are antiferromagnetic direct exchange and a factor 4 smaller in MnN and a factor 2 smaller in \( \text{Mn}_3\text{N}_2 \). The \( c/a \) reduction in MnN is clearly correlated with the magnetic ordering: the magnetoelectric coupling provides a way to break the frustration of multiply degenerate ground states of the Heisenberg Hamiltonian with this type of interactions. We also found from our results for \( \text{Mn}_3\text{N}_2 \) that next-neighbor interactions without intervening \( \text{N} \)
are much smaller, essentially zero. The Heisenberg model proposed appears to give a fairly good fit to a range of different magnetic configurations that we studied. Longer range interactions were considered but found to be negligible. Distinguishing different types of nearest-neighbor interactions in Mn$_3$N$_2$ also seemed an unnecessary refinement. We find that in going from MnN to Mn$_3$N$_2$ the reduction in the number of second-nearest-neighbor double exchange $J_2$ interactions is compensated by an increase in the nearest-neighbor direct exchange $J_1$ by a factor 2 while the second nearest neighbor interactions stays about the same. This indicates a stronger direct Mn-Mn bonding in Mn$_3$N$_2$, which is consistent both with the shortening of interatomic distances obtained from our structural relaxation calculations, in good agreement with experiment, and with the changes observed in the partial densities of states. In spite of this compensation, the mean field approximation predicts the Néel temperature of Mn$_3$N$_2$ to be slightly lower than that of MnN, in disagreement with experiment. Effects beyond mean field were estimated based on Monte Carlo results in literature for the Ising model with second-nearest-neighbor ferromagnetic and nearest-neighbor antiferromagnetic interactions and indicate that the conclusion should hold up beyond mean field theory and furthermore seem to provide a good estimate of the actual Néel temperature in MnN. On the other hand, these Monte Carlo simulations suggest possibly a second order phase transition. Since there is no direct evidence of the magnetic nature of the observed phase transition at 925 K in Mn$_3$N$_2$, we suggest that it may be related to N disorder rather than the AFM-paramagnetic transition and that the latter has not yet been observed in Mn$_3$N$_2$. Our work suggests simulations of Heisenberg Hamiltonians of the type considered here would be valuable. Most of all, though, further experimental investigation of Mn$_3$N$_2$, in particular a temperature dependent neutron diffraction study in the neighborhood of 500–600 K is needed, as well as a study of the N ordering at higher temperatures. A systematic study of the Néel temperature in $\theta$–MnN$_{1-x}$, as a function of N concentration would also be of considerable interest. We have not yet touched upon the more difficult questions of the orientation of the magnetic moments and magnetic anisotropy, which require inclusion of spin-orbit coupling in the calculations. This is reserved for future work.

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