Effects of vacancies and impurities on the relative stability of rocksalt and zincblende structures for MnN

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Using density functional calculations, it is shown that pure MnN is stable in zincblende rather than in the experimentally reported distorted rocksalt structure. However, about 4% N vacancies are found to stabilize the rocksalt structure. It is found that C and O substitutions on N and Ga on Mn also favor rocksalt but N, S, Fe, and Co stabilize zincblende. This suggests that zincblende MnN can possibly be grown under N-rich condition with controlled doping of S, Fe, and Co.

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I. INTRODUCTION

Manganese nitrides have been studied for decades because of the richness of the Mn-N phase diagram and the variety of their magnetic properties. A renewed interest in MnN has occurred in recent studies of dilute magnetic semiconductors because MnN might occur as a secondary phase during the epitaxial growth of Mn doped nitride semiconductors, such as GaN, AlN, and InN. From this point of view, it is of interest to better understand the phase stability and structural preference of MnN. MnN is found experimentally to occur in a distorted rocksalt (RS) structure which is antiferromagnetic (AFM) and metallic. The structure is distorted in the [001] direction by a c/a ratio of 0.98, which was shown to be related to the AFM order.

Although several computational studies have been performed based on first principles density functional methods for MnN, few of them compared the energy difference between different structures. Shimizu et al. found all the 3d transition metal (TM) nitrides to prefer the RS structure, which is in contrast to the results that FeN and CoN were reported to have the zincblende (ZB) structure as ground state in both experimental and theoretical studies. Using the full-potential linearized muffin-tin orbital (FP-LMTO) method, Miao and co-workers studied the relative stability of ZB and RS throughout the 3d series as a function of lattice constant. It was found that the early TM nitrides prefer RS and the later ones ZB, and lattice expansion favors ZB. The transition from RS to ZB stable structures occurs for MnN; i.e., the ground state of MnN was found to be ZB and the RS structure became the preferred state only under 4% compression. Being right at the transition, the energy difference between the two structures is quite small for MnN, only 0.2 eV/f.u. The recent first principles pseudopotential calculations performed by Hong et al. also confirmed that MnN is globally stable in the ZB structure. Yet, there have been no experimental reports of ZB MnN. In this paper, we address potential reasons for this and possible pathways to stabilize this phase in MnN.

At present, it is not clear whether the origin of this discrepancy between theory and experiment is due to experimental or computational inaccuracies. First, the calculations used the local spin density approximation, which is known to contract the lattice and stiffen the bonds and may have problems for systems containing localized d electrons. On the other hand, most MnN samples have sizable concentration of nitrogen vacancies and a tendency to lose N at higher temperature. In fact, the phase of MnN is sometimes labeled as MnN$_{5-x}$, rather than MnN. Thus, vacancies could be stabilizing the RS structure.

In this work, we first check the total energy calculations for MnN in both ZB and RS structures using different exchange-correlation functionals. Second, we calculate the total energies of MnN in the ZB and RS structures with various concentrations of N vacancies. Finally, we study other impurities and interstitial N and their effects on the relative stability of ZB and RS and attempt to explain these results in terms of known theories on the relative stability of ZB and RS in TM nitrides.

II. COMPUTATIONAL METHOD

The basic methodology followed in this work is density functional theory. The Kohn-Sham equations are solved using the linearized muffin-tin orbital (LMTO) method. For most of the calculations, we used the FP-LMTO method, which does not make any shape approximations to the potential or charge density and allows for accurate calculation of the forces and hence structural relaxation in an all-electron approach. Several exchange-correlation functionals are used to test the robustness of our earlier prediction that ZB would be the ground state of MnN. We used the von Barth–Hedin (vBH), the Ceperley-Alder (CA), and the Perdew-Wang 91 generalized gradient approximated (GGA) functionals. The latter is currently only available in the atomic-sphere approximation (ASA) of our LMTO codes, while local-density approximation (LDA) is available in both ASA and FP-LMTO. Therefore, we also studied the differences between FP-LMTO and ASA in the LDA. For the highly symmetric structures (zincblende and rocksalt), the ASA is actually quite accurate if empty spheres are introduced in the usual manner.

The major part of the paper concerns the effects of vacancies and other point defects on the relative stability of the two structures. To study these defects, calculations are performed for supercells that contain 32 Mn and 32 N atoms. Using the same supercell, we performed calculations for MnN in ZB and RS structures with 0, 1, 2, 4, or 8 nitrogen vacancies and a tendency to lose N at higher temperature.
vacancies. The vacancies are uniformly distributed over the cell, such that their distance to each other are approximately the same. The advantage of using a constant supercell size for different concentrations is that it makes the comparisons of the total energy for different vacancy concentrations more accurate. With the same unit cell and \( k \)-point mesh, numerical errors caused by the integrals in momentum space are expected to cancel out to a large degree. A \( 4 \times 4 \times 4 \) \( k \) mesh is used to ensure adequate convergence. The \( \nu \)BH exchange and correlation functionals are used for the supercell calculations.

III. RESULTS

Figure 1 shows the cohesive energies of MnN in the ZB and RS structures calculated using different combinations of the exchange-correlation functionals and the LMTO methods. Both within GGA and LDA ZB are found to be lower in energy than RS by about 0.2–0.3 eV. Although there are small quantitative differences between the different exchange-correlation treatments, and between ASA and FP-LMTO for the same exchange-correlation function, the basic conclusion on which structure is the equilibrium one stays the same. The present calculations are done for the ferromagnetic states only. The antiferromagnetic coupling for neighboring layers along the [001] direction for the RS structure and the corresponding strain relaxation along the [001] direction can lower the energy of the RS structure. However, this energy caused by the magnetic coupling is significantly smaller than 0.1 eV and will not change the conclusion that ZB is more stable.\(^8\) LDA calculations, FP or ASA, obtain RS lattice constants slightly smaller than 4.0 Å that is about 5% smaller than the experimental value. The ASA GGA calculations give a lattice constant of about 4.1 Å, which is still 3% smaller than the experimental values. For the ZB structure, both GGA and LDA, gave an equilibrium lattice constant of 4.2 Å.

Figure 2 shows the total energies for MnN in the ZB, RS, and AFM distorted RS (R1) structures for various nitrogen vacancy concentrations.

The existence of the nitrogen vacancies at the level of a few percent cannot be excluded in the RS MnN samples synthesized by Suzuki et al.\(^6\) by a reactive sputtering method in \( \text{N}_2 \) gas, a method which lacks N activation. The (unstated) error bar in their chemical analysis method is likely to be of the order of a few percent. Yang et al.\(^7\) using molecular beam epitaxy with a nitrogen plasma source, provided evidence of a closer to ideal Mn:N ratio of 1:1 but grew their samples as very thin films on a MgO substrate, which may have assisted in stabilizing the rocksalt structure.

It is interesting to note that the AFM distorted RS structure is predicted to be slightly higher in energy than the FM RS for pure MnN near the calculated equilibrium volume. However, when adding about 4% vacancies, the AFM state becomes lower than the FM one, in agreement with experiment.

The energy of formation of the nitrogen vacancy for phase \( \alpha \) (RS or ZB) is defined as

\[
\Delta E_f(\alpha) = E[D, \alpha] - E[C, \alpha] + \mu_N,
\]

with \( \mu_N \) the chemical potential of N and \( E[D, \alpha] \) and \( E[C, \alpha] \) are the binding energies of the defect containing cell and perfect crystal cell, respectively, relative to the energy of the free atoms. In the N-rich limit, the chemical potential of N is taken to be half the (experimental) binding energy of a \( \text{N}_2 \) molecule, or \(-4.9 \) eV,\(^{25}\) while in the Mn-rich limit, \( \mu_{\text{Mn}} \) is taken to be the binding energy in bulk fcc Mn, calculated to be \(-2.7 \) eV and in good agreement with experimental data (\(-2.94 \) eV).\(^{26}\) With our calculated cohesive energy of \(-15.9 \) eV for MnN, this gives as energy for formation from
bulk Mn and N\textsubscript{2}, \(\Delta H_f(\text{MnN})\) =–8.3 eV. The excess chemical potentials \(\bar{\mu}_i = \mu_i - \mu_i^{ref}\) are defined with respect to these reference states. To form MnN, the excess chemical potentials of the Mn and N atoms should satisfy the condition, \(\bar{\mu}_{\text{Mn}} + \bar{\mu}_{\text{N}} = \Delta H_f(\text{MnN})\), and the allowed ranges of Mn and N excess chemical potentials are \(\Delta H_f(\text{MnN}) \leqslant \bar{\mu}_{\text{Mn}} \leqslant 0\) and \(\Delta H_f(\text{MnN}) \leqslant \bar{\mu}_{\text{N}} \leqslant 0\). The variation of the formation energy with the N chemical potential is shown in Fig. 3. It reveals that under nitrogen-rich condition, the nitrogen vacancy formation energy is 5 eV for RS structure and 9 eV for ZB structure. However, under relative N-poor condition, the formation energy becomes negative for RS structure, indicating that the system prefers to accommodate vacancies. For ZB structure, the formation energy stays positive even under extreme N-poor condition, although it can be as low as 0.5 eV.

The above calculated formation energies are obtained from 64 atom supercells with one vacancy, corresponding to a concentration of about 3%. However, it is worth noting that the calculated formation energy changes vary only slightly with the concentration and thus correspond essentially to the dilute limit. This can be clearly seen from Fig. 2. The total energy for ZB, RS, and AFM RS almost fall on straight lines, respectively. This indicates that the energy cost is proportional to the concentration and justifies the identification of the energy per vacancy in these cells with the dilute limit of the energy of formation. This also indicates that the interactions between the vacancies are small and very short range even though the system is metallic. We can then, in principle, obtain the minimum concentration of vacancies to stabilize the RS structure from

\[
 x_{\text{min}}(\Delta E_f(\text{RS}) - \Delta E_f(\text{ZB})) = E_{\text{ZB}} - E_{\text{RS}},
\]

where the \(E_{\text{ZB}}\) and \(E_{\text{RS}}\) are the binding energies of MnN taken at zero concentration of vacancies. This gives \(x_{\text{min}} = 0.043\), close to the direct observation shown earlier and independent of the choice of chemical potential.

In Fig. 4, we show the partial density of states (PDOS) of the Mn atom next to the vacancy in comparison with the Mn atom far away from the vacancy, in the energy range of mostly Mn\textit{d}–N\textit{p} antibonding states. One can see that the changes in PDOS caused by the vacancy are more profound in the ZB than in the RS structure. This is essentially because in RS, the \(e_g\) orbitals, which form \(\sigma\) bonds with the N, and

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**FIG. 3.** (Color online) N vacancy formation energies with different N chemical potentials.

**FIG. 4.** (Color online) Partial density of states for MnN in the ZB and RS structures with N vacancies. The black solid lines show the total density of states (DOS) for Mn atoms around the vacancy. The area shaded by pink pattern lines descending from left to right shows the partial DOS of Mn \(d\) states with \(s\) symmetry, and the area shaded by green pattern lines rising from left to right show the states of \(t_2\) symmetry. The dashed lines show the total DOS of Mn far from the vacancy.

are therefore most directly affected, occur far away from the Fermi level as bonding or antibonding states, while in ZB, \(e\)– and \(t_2\)-like states are more mixed up near \(E_F\). It is not straightforward to interpret the change in total energy in terms of these PDOS changes because other terms than the band structure come into play. Nevertheless, one may note that in ZB, there is as strong depression of occupied PDOS in the minority spin channel in the range of \(-2\) eV to the Fermi level and an increase in \(e\)-like states above \(E_F\) which would raise the sum of occupied one-electron energies. Thus, this can at least partially be held responsible for the energy cost of forming nitrogen vacancies in the ZB. In the RS, no such effect is discernible, which would partially explain why vacancies form more easily in RS and hence favor the RS over the ZB structure.

We can also see in Fig. 4 that in ZB, there is a much smaller splitting between up and down spin states, consistent with the small magnetic moment in MnN.\textsuperscript{16} Examining the magnetic moments in ZB in more detail, we also observe an increase in magnetic moment for the Mn near the vacancy in ZB, consistent with the PDOS changes. We can see in Fig. 4 that there is a gap just above \(E_F\) for majority spin states, making the system close to a half-metal. This only occurs when we add vacancies in ZB-MnN. Thus, ZB-MnN containing vacancies or other magnetic impurities might be interesting as a magnetic material, but we have not yet investigated whether the system prefers ferromagnetic or antiferromagnetic alignment. This is rather difficult to ascertain if the moments are so small and taking into account the disorder aspects. Furthermore, the desire to make ZB-MnN ferromagnetic and stabilizing ZB-MnN in the first place appear to be in conflict with each other, since the latter requires suppressing the vacancies.

Because most of the commonly used semiconductors have tetrahedrally bonded structures, ZB MnN could give a better interface matching, which could be useful for metal semicon-
The chemical potential of N is taken as $-8.7$ eV which is neither at N-rich nor at N-poor condition.

Table I, the formation energy of GaMn is significantly lower than ZB vs RS structure in the TM nitrides was given by Eck et al. The substitutions do have lower formation energies in ZB MnN.

Ga atom which tends to be tetrahedrally bonded with the surrounding N atoms. On the other hand, Fe and Co substitutions can significantly stabilize the ZB structure. Our calculations suggest that one might achieve this goal by controlling the growth condition to avoid the formation of N vacancies in the sample. On the other hand, other impurities might assist in stabilizing the ZB structure. Our search includes anion impurities, such as C, S, and O substitutions at N sites, N interstitials, and cation impurities, such as Ga, Fe, and Co substitutions at the Mn site. Table I shows that the C and O substitutions have lower formation energies for RS MnN and will stabilize it. The N interstitial, however, does show a lower formation energy for ZB structure. However, the formation energy of N$_i$ is high. Only under extreme N-rich condition, the formation energy of N interstitials can be lowered to 0.13 eV for ZB structure and 1.88 eV for RS structure. There are actually two different interstitial sites in ZB structure, the tetrahedral and the octahedral sites, but as shown in Table I, their formation energies differ only slightly.

For cation impurities, we notice that the nitrides of Ga, Fe, and Co are stable in either wurtzite or ZB structures. The energy difference between the wurtzite and the RS structures for GaN can be as large as 0.7 eV/f.u. However, as shown in Table I, the formation energy of Ga$_{\text{Mn}}$ is significantly lower for RS structure, which is in contrast to the bonding nature of Ga atom which tends to be tetrahedrally bonded with the surrounding N atoms. On the other hand, Fe and Co substitutions do have lower formation energies in ZB MnN.

An interesting discussion of the relative stability of the ZB vs RS structure in the TM nitrides was given by Eck et al., using the concept of crystal orbital Hamilton population (COHP). This analysis is based on a partitioning of the band structure energy into contributions from different bonds. It allows one to discern bonding and antibonding regions for different atomic orbital pairs. They found that the relative stability of RS vs ZB is decided not so much by the N-TM interactions but by the TM d-d interactions. In a rigid band structure view, only the bonding states are filled for early TMs, and therefore, the RS structure is more stable. In contrast, for late TMs, the antibonding states are also filled, therefore weakening the d-d interactions in RS structure and destabilizing it. Based on the COHP analysis, they predicted that MnN would be stable in the ZB structure.

We found that the behavior of most of the impurities in Table I can be understood from this point of view. Because the electrons have started to fill in the antibonding states in MnN, an electron density increase will destabilize the RS structure, and conversely, any electron decrease will stabilize RS. Among the impurities shown in Table I, S$_N$, N$_i$, Fe$_{\text{Mn}}$, and Co$_{\text{Mn}}$ act like electron donors as they are rich in electrons. Therefore, they should favor the ZB structure. On the other hand, C$_N$ and Ga$_{\text{Mn}}$ remove electrons and stabilize the RS structure. We emphasize that the word donor here is used in a chemical sense not in the sense of inducing shallow impurity levels in the gap of a semiconductor. MnN is, in fact, found to be metallic both in the ZB and RS phases. Mn in MnN can be considered to be trivalent and thus isovalent with Ga in terms of sp bonding, but Ga would lack the d-valence electrons and thus reduce the effective number of electrons in the d bands, so that the band filling is more as in the early transition metals which favor RS. However, the behavior of V$_N$ and O$_N$ cannot be understood from this point of view. Both impurities are donors, yet favor the RS structure. Considering the strength of the Mn-N and Mn-O bonding that are involved in these two impurities, the relative stability of RS and ZB structures in these cases appears to be caused by the cation-anion bonding. Due to the strong changes of such bonding states, the rigid band view might not hold.

### IV. CONCLUSIONS

In conclusion, our first principles calculations show that MnN is thermodynamically stable in the ZB structure, provided the system has less than 4% nitrogen vacancies. Comparison of several LDA and GGA exchange-correlation functionals confirms this earlier finding. Impurities, such as C and O substitutions at anion or Ga at cation sites, can also stabilize the RS structure. On the other hand, N interstitials, S (on N), and Fe or Co (on Mn) substitutions can significantly stabilize the ZB structure. The effects of most of these various impurities can be understood in a rigid band picture in terms of electron donation or removal from the d bands, which strengthens (weakens) the d-d bonding preferentially in RS. However, O$_N$ and V$_N$ affect the Mn-N binding too strongly and are also found to favor rocksalt. Therefore, we suggest that the growth of ZB MnN would be facilitated under N-rich conditions and with controlled doping of S, Fe, or Co.

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