Magnetic isomers and local moment distribution in Mn_5O and Mn_6O clusters

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A synergistic approach combining the experimental photoelectron spectroscopy and theoretical electronic structure studies is used to demonstrate the existence of magnetic isomers as well as configurations having comparable binding energies, identical spins, and yet differing in the distribution of local moments (called isomags). Our studies carried out on Mn_5O and Mn_6O clusters show that while the O atom occupies either bridge or hollow site with a binding energy of 6.88 eV in Mn_5, it prefers a hollow site with a binding energy of 7.18 eV in Mn_6 clusters. Mn_5O is shown to possess two magnetic isomers with total spins of 13 and 5 μ_B that contain three and five isomags, respectively. Mn_6O possesses three isomers, two with moments of 8 and 2 μ_B and a nonmagnetic. It is shown that the isomags, although undetected in magnetic experiments, can be identified via their electronic structure in experimental photoelectron spectra.

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I. INTRODUCTION

Finite size, preponderance of surface atoms, flexible geometrical arrangements, and the wider range of compositions are the unique features that permit small clusters to display structures, electronic and magnetic properties, and chemical behaviors that are different from those in the bulk.[1] Icosahedra1 configurations,[2] electronic shell structure and the associated magic numbers,[3] space quantization,[4] resonance quantum tunneling of magnetization,[5] and superparamagnetism[6–9] are just a few examples of the novelties in clusters. One of the most striking features in small clusters is the possibility of isomers.[10] Here, the ground state of a cluster can sometimes be marked by different geometrical arrangements of atoms that have comparable binding energies. There are even examples where the barriers separating these isomers are small and a cluster can convert from one geometrical shape to another even under ordinary thermal conditions.[11] For clusters of elements that exhibit magnetic order, the concept of isomers is conventionally extended to include different magnetic moments.[12] One such example is Cr_n clusters where the existence of magnetic isomers was demonstrated via the Stern-Gerlach deflection profiles almost ten years ago.[13] The present paper presents situations that require further extension of the concept of magnetic isomers. We demonstrate the possibility where a state of a given total spin multiplicity further has several different magnetic configurations that have comparable energies but different spatial distributions of local atomic moments. We refer to these as isomags. Here, we show the presence of magnetic isomers in Mn_5O and Mn_6O and isomags in Mn_5O. It is argued that their presence could lead to interesting magnetic excitations in bulk dilute magnetic semiconductors.

The manganese atom, with an electronic configuration of $3d^5 4s^2$ has a closed *s* shell and a half-filled *d* subshell and a spin multiplicity of 6 in the ground state. The unfilled *d* states are about 4.40 eV above the filled *d* state indicating that the atomic moment of 5 μ_B is fairly stable. In small clusters with reduced mixing between -*d* and -*s* states, the magnetic coupling between atomic moments is relatively weak and in a recent paper[14] we have shown that the ground state of free Mn_5 and Mn_6 clusters are marked by isomers. For Mn_5, these isomers correspond to cluster magnetic moments of 3, 13, and 23 μ_B, respectively, while for Mn_6, the isomers have magnetic moments of 2, 8, 16, and 26 μ_B respectively.

The purpose of this paper is to examine if the magnetic coupling in Mn_n clusters[14,15] can be controlled by adding impurities and their effect on the magnetic configurations. Apart from an intrinsic interest, there is another motivation for such a study. It is now known that wide band-gap semiconductors such as GaN, when doped with Mn, exhibit ferromagnetic order.[16] This has generated considerable excitement in the field of dilute magnetic semiconductors. It is suggested that the Mn impurities cluster around the N atoms and it was recently proposed that the ground states of Mn_nN clusters are all ferromagnetic with large moments of 5 μ_B per atom.[17] Similar dilute magnetic semiconductors are also being envisioned for Mn doped oxide semiconductors. It is therefore interesting to examine the effect of O on the magnetic moment and coupling in Mn_5 and Mn_6. As we proposed earlier, the magnetic moments of clusters can be probed by negative ion photoelectron spectroscopy (PES). We have, therefore, also carried out such experiments in this work. To make contact with these experiments, the theoretical studies included neutral as well as anionic Mn_5O^- and Mn_6O^-.

In Sec. II, we describe the details of our method while Sec. III is devoted to a discussion of results. Finally, Sec. IV contains the conclusions of this work.

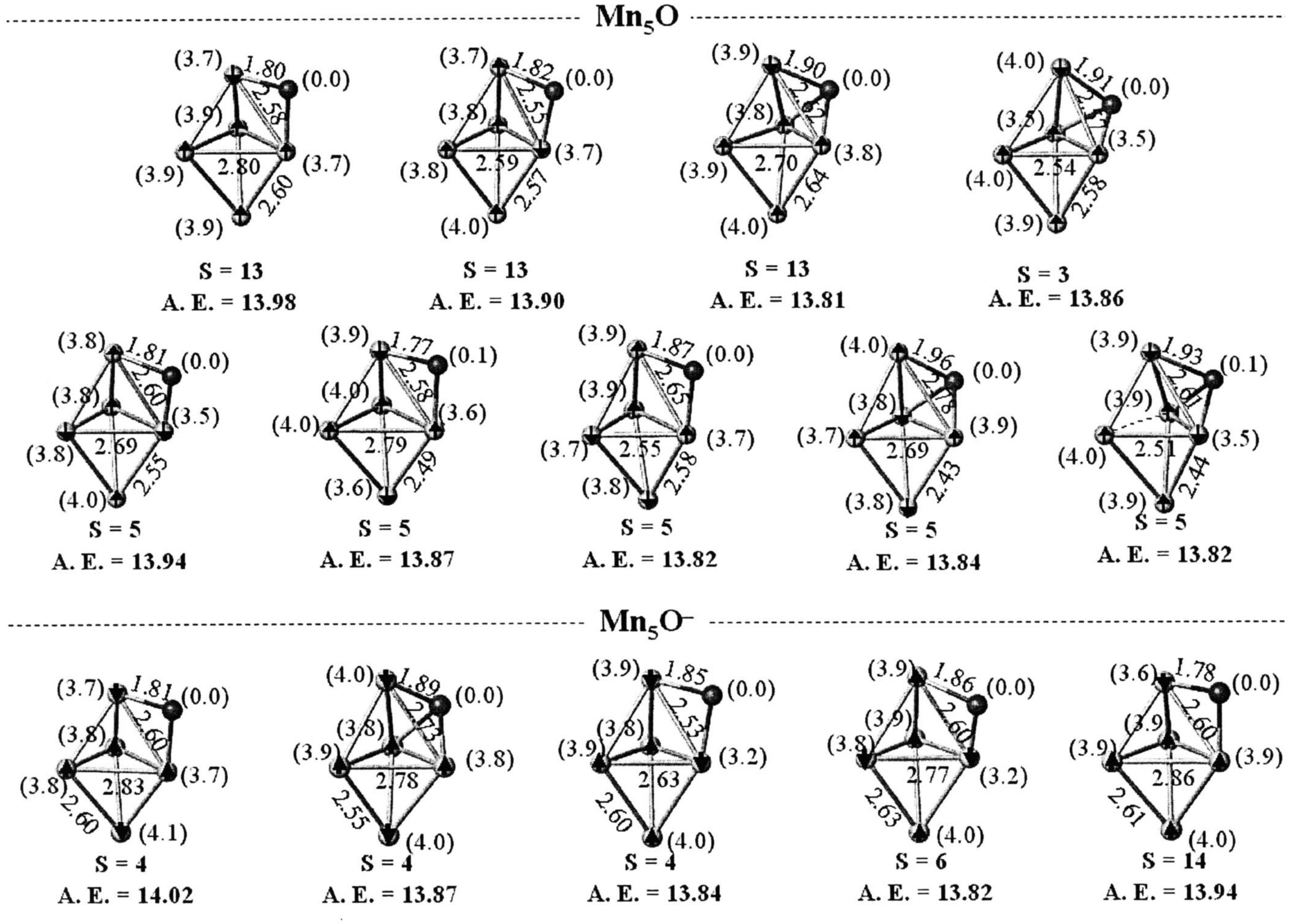

FIG. 1. Ground state geometry and some of the low lying isomers/isomags for the neutral and anionic Mn_5O clusters. The arrows ↑ and ↓ indicate the direction of spin polarization at each site and the corresponding atomization energy (AE) and magnetic moments (in μ_B) are given within parenthesis at each site. The bond lengths are in Å.

II. DETAILS OF CALCULATIONS

The theoretical investigations were carried out within a linear combination of atomic orbitals molecular orbital framework where the exchange correlation contributions are implemented using gradient corrected density functional.[18] The actual studies used the Naval Research Laboratory Molecular Orbital Library (NRLMOL) developed in the group of one of the authors.[19,20] The basis sets in this scheme are Gaussian functions and the integrals are carried out numerically over a mesh of points. The basis set for Mn consisted of 7*s*, 5*p*, and 4*d* functions constructed from 20 bare Gaussians and that of O had 5*s*, 4*p*, and 3*d* functions constructed from 13 bare Gaussians.[21] The basis set was supplemented by 1 *d* Gaussian. All geometries were optimized fully with Hellmann-Feynman forces smaller than 0.001 hartree/bohr. As we will show, the ground state of the oxidized cluster corresponds to ferrimagnetic configurations. In these situations, one has to examine all possible ferrimagnetic states, in addition to the various geometrical arrangements.

III. RESULTS AND DISCUSSION

As shown in a recent paper,[14] the ground state of a free Mn_5 is a triangular bipyramid structure while that of an Mn_6 is an octahedral arrangement of atoms. To understand the effect of oxidation, an O atom was brought toward the free clusters in on-top, bridge, and hollow configurations. For each situation, we examined the possible configurations (up and down orientation of the local atomic moments). The positions of atoms and the total spin were optimized for each configuration. As mentioned before, we have also carried out negative ion photoelectron spectroscopy measurements on Mn_5O^- and Mn_6O^- clusters. To make contact with these experiments, the corresponding calculations on clusters containing an extra electron were also carried out.

Figure 1 shows the ground and the low energy configurations of the neutral and anionic Mn_5O clusters whose total energies are within 0.2 eV of the ground state. Also given is the atomization energy (AE)

$$\mathrm{AE} = nE(\mathrm{Mn}) + E(\mathrm{O}) - E(\mathrm{Mn}_n\mathrm{O}),$$

representing the energy required to break the cluster into atoms. Here $E(\mathrm{Mn}_n\mathrm{O})$ is the total energy of the cluster, and $E(\mathrm{Mn})$ and $E(\mathrm{O})$ are the total energies of the Mn and O atoms. For the anionic clusters, the energy is calculated for breaking into neutral atoms and an O^-. Note that the ground state corresponds to the O atom occupying a bridge site. The binding energy of the O atom to the Mn_5 cluster is 6.88 eV compared to the atomization energy of 7.10 eV for the entire Mn_5 cluster. This shows that there is a strong chemical bond between the Mn atoms and O. The strong chemical bond also affects the magnetic structure of the cluster. The first effect is the destabilization of the ferromagnetic state. As mentioned before, pure Mn_5 has a ferromagnetic structure with a magnetic moment of 23 μ_B that is only 0.02 eV above the ground state. The addition of oxygen destabilizes the ferromagnetic solution taking it to 0.76 eV above the ground state. The other interesting effect is the occurrence of magnetic configurations that correspond to the same total spin, that are energetically close, but have different arrangements of the local magnetic moments. As shown in Fig. 1, Mn_5O has two structures with spin moment of 13 μ_B and three structures with spin 5 μ_B, where O occupies the bridge site. When O occupies a hollow site in Mn_5O, there exists one structure with a spin moment of 13 μ_B, two structures with a spin moment of 5 μ_B, and one structure with a spin moment of 3 μ_B. We refer to the configurations with same total spin and different local arrangements as the isomags in analogy with isomers, isotherms, isobars, etc. To summarize, Mn_5O then has three groups of magnetic isomers with spins of 13, 5, and 3 μ_B. The isomers with moments of 13 and 5 μ_B have 3 and 5 isomags, respectively.

The corresponding results for Mn_6O are shown in Fig. 2. Note that the O atom prefers to occupy a hollow site. The binding energy of the pure Mn_6 increases by 7.18 eV due to the addition of a single O. An investigation of the states with different spin multiplicities shows that the cluster has only three isomers with magnetic moments of 0, 2, and 8 μ_B. The ferromagnetic state of pure Mn_6 with a magnetic moment of 26 μ_B is highly destabilized by the addition of O and is 0.50 eV above the ground state. Can the isomags and isomers of Mn_5O and Mn_6O be seen in actual experiments?

The conventional approach to measure the magnetic moments of clusters is to deflect them via an inhomogeneous magnetic field in a manner similar to that used for demonstrating space quantization in the Stern-Gerlach experiment.[6–9] Here, the magnetic clusters are passed through a gradient magnetic field. The mean magnetic field helps align the magnetic moments while the gradient of the magnetic field generates a force deflecting the clusters from their straight path. Such an approach has been used to determine the magnetic moments of Fe_n, Co_n, and Ni_n clusters. As explained in a recent paper,[14] while such an approach works for Fe_n, Co_n, or Ni_n, it enters into difficulty for Mn_n where the exchange coupling between the atomic moments is weak. An alternate approach, outlined by the present authors, is to use the negative ion photoelectron spectroscopy based on measuring the electronic transitions between the anions and the neutral clusters.[22,23] The basic idea is to subject selected cluster anions to a laser beam of fixed photon energy and then to measure the electron binding energies (EBES) of the photodetached electron. The difference between the energy of the photon and that of the detached electron then yields the binding energy of the electron. Suppose that an anionic cluster has N unpaired electrons and hence a multiplicity of $M=N+1$. When the electron is detached, the neutral cluster will have a spin multiplicity of $M-1$ or $M+1$, depending on whether the electron is removed from the majority or the minority state. The photoelectron spectra correspond to a plot of the electron intensity versus energy of the detached electrons. The peaks in the photoelectron spectra corresponding to the two kinds of transitions can be compared with theoretical calculations where one first determines the ground state of the anion including its spin multiplicity and then the energies to make the transition to the neutral ground and excited electronic states with multiplicity $M-1$ or $M+1$. Quantitative agreement between the calculated energies and electron binding energies of the experimental peaks strongly suggests that the spin multiplicity calculated from theory is correct. Knowing the spin multiplicity, one can find the spin magnetic moment. Earlier, we proposed[23] such a procedure to identify the ground state of Fe_3. Tono *et al.*[24] have recently used it to characterize the ground state of Cr_2O.

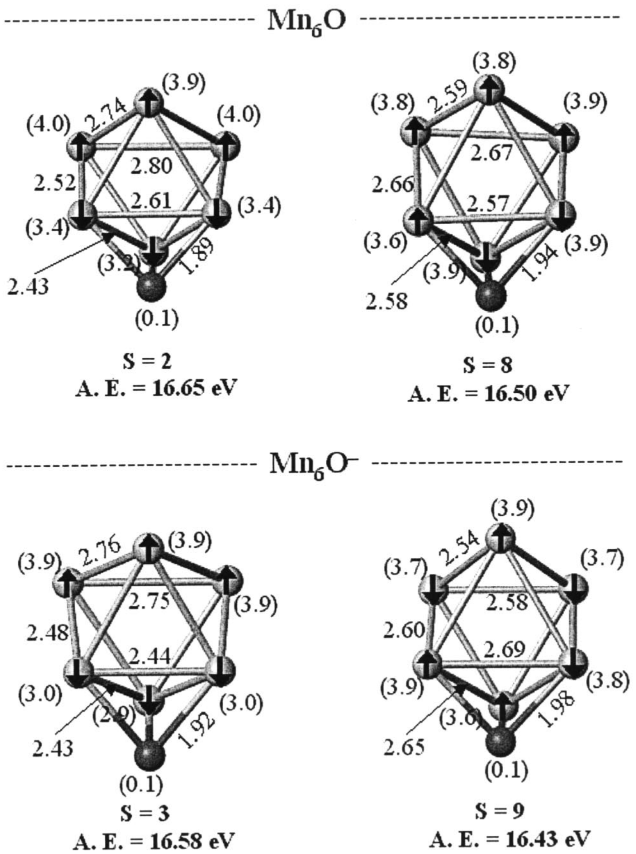

FIG. 2. Ground state geometry and some of the low lying isomags for the neutral and anionic Mn_6O clusters. The arrows ↑ and ↓ indicate the direction of spin polarization at each site. The corresponding AE and the magnetic moments (in μ_B) are given within parenthesis at each site. The bond lengths are in Å.

In this work we have measured the photoelectron spectra of Mn_5O^- and Mn_6O^- anions. These are shown in Fig. 3. For details of the experimental setup, the generation of anions, and the measurement of the kinetic energy of the detached electrons, the reader is referred to the earlier papers.[22] Here we focus mainly on the results. Note that the photoelectron spectra of Mn_5O^- is marked by intense peaks around 2.1,

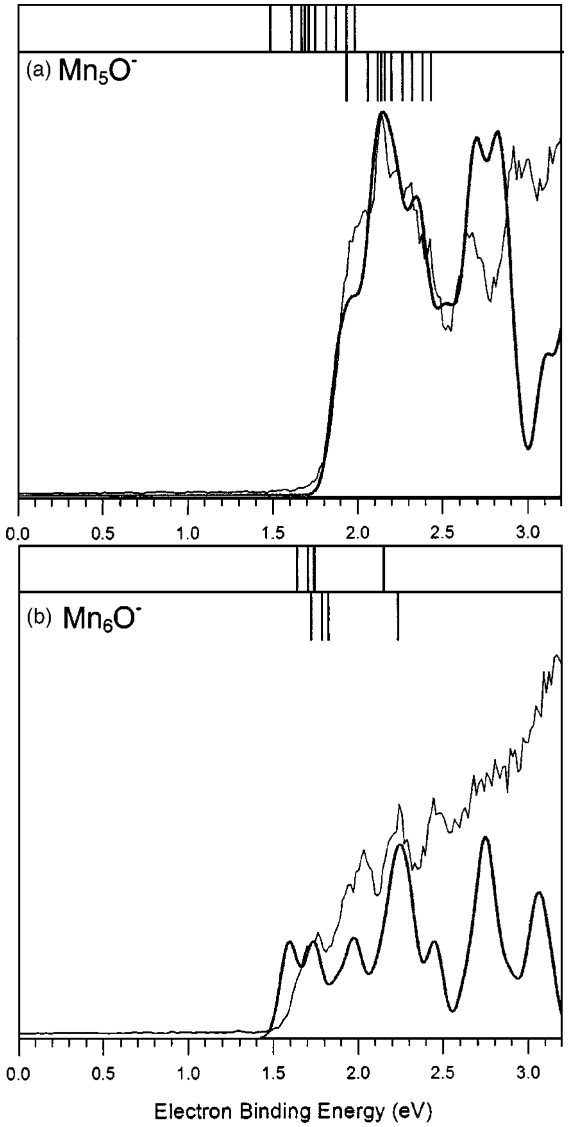

FIG. 3. The experimental negative ion photoelectron spectra for Mn_5O^- and Mn_6O^- (finer lines). The vertical bars in the upper panels are the theoretical transition energies from the anions to the neutral clusters. The figures also show that a small constant shift can reproduce the experimental peak. Also shown are the calculated DOS in the corresponding anions (thicker lines).

2.6, and 2.9 eV. One of the notable features of the current spectra is that the primary region (1.5–2.0 eV) is marked by several peaks (one can notice three close shoulders/subpeaks around EBES of 1.95 eV). Even the region following the first peak is marked by numerous secondary peaks. The spectra of Mn_6O^- shows a first set of peaks around 1.70 eV, followed by a first major peak around 2.0 eV.

To make contact with these experiments, we calculated the ground state geometry and spin multiplicity of Mn_5O^- and Mn_6O^-. These are shown in Figs. 1 and 2. Mn_5O^- has three isomers corresponding to the spin magnetic moments of 4, 6, and 14 μ_B. Further, the isomer corresponding 4 μ_B has 3 isomags. Mn_6O^- has 3 isomers with total spins of 1, 3, and 9 μ_B.

In order to compare the theoretical predictions with the experimental, PES spectra, we used two different approaches that are currently used. One of these is to calculate the vertical transitions from the anion with a multiplicity of M to neutral clusters with multiplicity of $M-1$ and $M+1$. The difference in the total energy of the anion and neutral clusters are then related to the position of peaks in the photoelectron spectra. While such an approach provides absolute position of the peaks, one has to consider all the excited states of the neutral clusters with a given multiplicity to obtain the entire spectra. In the present case, one has to repeat it for all isomers. An alternate approach,[25] now routinely used, is to compare the density of electronic states of an anion with the experimental spectra. Unfortunately, this does not provide the absolute position of the peaks. It is then customary to match the position of the first shoulder or peak to the experimental spectra and then compare the remaining spectra.

For Mn_5O^-, the calculated adiabatic electron affinity which corresponds to the difference in energy between the ground state of the anion and the ground state of the neutral cluster, is 1.64 eV which is close to the left tail of the experimental spectra. For the anion isomers (isomags) in Fig. 1, the transition energies lie at 1.49, 1.61, 1.67, 1.69, 1.71, 1.75, 1.81, 1.87, 1.94, and 1.98 eV and in Fig. 3 we have marked them by vertical bars in the upper panel. What is interesting is that a rigid shift of 0.45 eV of the bar code can fairly reproduce the spectra.

As mentioned before, an alternate approach[25] to analyzing the negative ion photodetachment spectra is to compare it with the density of state (DOS) in the anion. Such a comparison however requires positioning of the theoretical DOS. In this work, we used the following procedure to calculate the total density of states. In each isomag, the energy levels were broadened by placing a Gaussian of half width 0.07 eV at each of the energy levels. Further, the initial slope of the resulting density of states was positioned to match the initial rise of the experimental spectra. Finally the DOS of all the isomags were added. The final DOS is shown by the thick line in Fig. 3. Note that the calculated DOS reproduces the main features of the experimental spectra. We found that the presence of multiple peaks from 1.70 to 2.45 eV can only be accounted for by adding the DOS of all isomers/isomags as none of the individual DOS would account for the entire spectrum.

For Mn_6O^-, the experimental spectra shown in Fig. 3(b) has less structure than in Fig. 3(a). The calculated adiabatic electron affinity was 1.53 eV that is again close to the left shoulder of the experimental spectra. In Fig. 3 we show the absolute transition energies (vertical bars), transition energies obtained by a rigid shift of 0.27 eV as well as the DOS obtained by combining the one electron levels in the three isomers in Fig. 2. Our calculated theoretical peaks lie at 1.63, 1.70, 1.74, and 2.15 eV. These are in good agreement with the experimental subpeaks (Fig. 3) around 1.70 eV and the first peak around 2.2 eV. The DOS (shown by darker line) reproduce the entire spectra fairly well. The calculated isomers thus provide a reasonable explanation of the experimental photoelectron spectra. Combined with the earlier comparisons for Mn_5O^-, we can conclude that the isomers/isomags obtained in theory are seen in the PES spectra.

The presence of isomers/isomags in $\mathrm{Mn}_n\mathrm{O}$ is related to the weak interatomic exchange. It is now known that the magnetic coupling in pure Mn_n clusters changes with size.[15] While Mn_2 is van der Waal antiferromagnet, Mn_3 and Mn_4 exhibit ferromagnetic coupling. Mn_5 and Mn_6, as we showed in a recent paper,[14] are marked by energetically close ferromagnetic and ferrimagnetic arrangements. Our results show that this degeneracy is changed by O. First, the purely ferromagnetic states are destabilized by the addition of O. This is somewhat consistent with recent observation[26] that the addition of O reduces the magnetic moment of pure Mn_n clusters. Second, it leads to isomers/isomags of lower total magnetic moments. The weak interatomic exchange in Mn_n clusters is therefore not affected by the O atoms even though there is a strong electronic binding.

IV. CONCLUSIONS

To summarize, the present work demonstrates that small, oxidized manganese clusters exhibit several isomers/isomags. This raises an interesting issue for dilute magnetic semiconductors such as GaN doped with Mn where it is known that the Mn impurities substitute at the Ga sites. There is recent evidence[16] of similar ferromagnetic behavior for Mn impurities in ZnO where Mn substitutes for the Zn atoms. Further, Mn cluster around N or O sites. In all theoretical and experimental analysis of such systems, it has been presumed that the Mn_nX $(X=\mathrm{N},\mathrm{O})$ clusters have a well defined moment. The presence of isomers/isomags of different atomic spin magnetic moments suggests that such systems may exhibit spin glass behavior at higher Mn concentrations. It is interesting to note that spin-glass behavior has recently been observed[27] in $(\mathrm{Ga},\mathrm{Mn})\mathrm{N}$ systems with higher Mn content. It is hoped that the present studies would stimulate more investigations, in particular the role of isomags in magnetic semiconductors.

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