Energetic stability and magnetic properties of MnO in the rocksalt, wurtzite, and zinc-blende structures: Influence of exchange and correlation

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We investigate the relative energetic stability and the magnetic properties of MnO in the rocksalt (rs), wurtzite (wz), and zinc-blende (zb) structures using density-functional theory with different approaches to exchange and correlation: the semilocal generalized-gradient approximation (GGA), the GGA+U method with an additional on-site interaction U, and the spatially nonlocal hybrid functional HSE03 that accounts for screened exchange. In contradiction to experimental observations, GGA predicts the fourfold coordinated zb and wz structures to be energetically favorable in comparison to the sixfold-coordinated rs geometry. The use of the hybrid functional HSE03 improves the energetic stability of the rs structure but still fails to determine the correct ground state of MnO. This deficiency can be overcome by applying the GGA+U method with U ≳ 4 eV. The computed total energies are used to fit the nearest- and next-nearest-neighbor exchange coupling constants of a Heisenberg model Hamiltonian. Only for the GGA+U functional with U ≳ 4 eV, the coupling constants as well as the resulting critical temperature for the magnetic phase transition are in agreement with measured quantities. Therefore, we conclude that an appropriate treatment of the correlation effects in MnO and similar compounds is necessary not only for the electronic but also for the structural properties.

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I. INTRODUCTION

In the course of the search for new materials with possible applications in spintronics, manganese compounds have aroused great interest. Dilute magnetic semiconductors with Mn atoms as dopants are promising candidates for the concomitance of semiconducting behavior and room-temperature ferromagnetism. Besides III-V alloys such as Ga1−xMnxAs, research is focused on II-VI compounds, such as Zn1−xMnxO, since Mn2+ ions can be easily included in a II-VI environment. Whereas MnO crystallizes in the cubic rocksalt (rs) structure, ZnO exhibits the hexagonal wurtzite (wz) crystal structure. For low concentrations of MnO, the Mn atoms occupy Zn substitutional sites and are, therefore, included in a hexagonal environment (see, e.g., Refs. 5 and 6). However, by increasing the MnO content in the heterostructural alloy Zn1−xMnxO, one can expect a transition from hexagonal symmetry (for low Mn concentrations) to cubic symmetry (for high Mn concentrations). As an initial step toward the determination of the structural and electronic properties of heterostructural alloys by means of first-principles calculations, detailed knowledge about the end components ZnO and MnO in both crystal structures is essential. While the rs, wz, and also zinc-blende (zb) polymorphs of ZnO have been studied extensively, almost all calculations for MnO concentrate on the naturally occurring rs phase.

From the theoretical point of view, the description of transition-metal oxides such as MnO (or the very similar compounds FeO, CoO, and NiO) is notoriously difficult rendering them benchmark materials for the understanding of the interplay between orbital, spin, and lattice degrees of freedom. Despite its partially filled 3d states, rs-MnO is an insulator both in its paramagnetic and antiferromagnetic (AF) phases. The antiferromagnetic state below the Néel temperature of 118 K (Ref. 15) is characterized by the so-called AF2 ordering of the cation sublattice, i.e., a stacking of ferromagnetic (FM) (111) planes with opposite spin directions in adjacent layers. The magnetic phase transition is accompanied by a slight rhombohedral distortion of the cubic lattice along the [111] direction. The crucial difficulty for ab initio calculations stems from the fact that one has to deal with localized d electrons and itinerant s and p electrons (originating from the Mn 4s states and the oxygen atoms) simultaneously.

In contrast to CoO and FeO, the description of MnO (and also NiO) within density-functional theory (DFT) applying the local spin-density approximation (LSDA) or a semilocal generalized-gradient approximation (GGA) already yields a fundamental gap due to exchange and crystal-field splittings. Nevertheless, the gap is dramatically underestimated compared to experimental findings. Besides the neglect of the excitation aspect, which can be taken into account by means of a quasiparticle calculation in the GW approach, this is attributed to the inadequate description of the exchange and correlation (XC) effects for the strongly localized d electrons. For this reason, the transition-metal oxides were considered to be prototypical Mott-Hubbard insulators, i.e., materials with a gap which is due to the d-d intra-atomic Coulomb energy U. Later, it turned out that also O p and transition-metal s states contribute to the valence-band maximum (VBM) or conduction-band minimum (CBM), respectively, causing a classification as charge-transfer insulator. In the meantime, new or extended approaches such as self-interaction corrected, on-site Coulomb-repulsion corrected (e.g., LSDA+U), optimized-effective potential, or hybrid XC functional methods have been developed to overcome the deficiencies of the DFT-LSDA/GGA for the electronic properties. Nevertheless, the DFT-based approaches have seemingly proven successful...
for the understanding of the ground-state properties such as atomic geometry and magnetic ordering, confirming the experimentally observed AF2 antiferromagnetic ordering within the (rhombohedrally distorted) rs structure. Only the distortion angles are overestimated. 

Whereas usually several magnetic orderings have been investigated within the rs phase, the question if other crystal structures with other magnetic orderings give rise to lower total energies in the DFT-LSDA/GGA framework has not been answered so far. Recently, a remarkable structural anomaly of MnN has been found. Instead of the experimentally observed slightly distorted rs structure with an antiferromagnetic ordering of type I, DFT-GGA calculations favor the zb structure. This failure can be resolved by including the strong on-site Coulomb interaction of the d electrons by means of a GGA+U approach or using the B3LYP hybrid functional. In addition, a possible stabilization of rs-MnN by at least 4% N vacancies has been suggested. Gopal et al. claim, based on their DFT-LSDA studies, that MnO in a tetrahedrally coordinated wurtzite geometry is not unfavorable compared to rs-MnO. However, they give no explicit values for the relative energetic ordering of these two polymorphs.

In the present paper, we study the relative energetic stability and magnetic properties of MnO within the rs, wz, and zb structures using GGA, GGA+U, the Hartree-Fock approximation (HFA), and the hybrid functional HSE03. The influence of the nonlocality of XC is discussed as well as the description of strong-correlation effects by means of the on-site Coulomb interaction U. Six different magnetic orderings are investigated for each crystal structure. The resulting total energies are used to fit the parameters of a Heisenberg model and to compute the critical temperatures of the magnetic phase transitions.

The examined magnetic orderings are briefly introduced in Sec. II. The computational details of the total-energy calculations are given in Sec. III. In Sec. IV, the relative energetic order of the various magnetic arrangements within the considered crystal structures is discussed. Furthermore, the influence of the XC functional is investigated. In Sec. V, we provide a discussion of the influence of the magnetic ordering and the XC functional on the electronic structure. The coupling constants of the Heisenberg model as well as the critical temperatures are calculated in Sec. VI. Finally, in Sec. VII, a summary is given and conclusions are drawn.

II. MAGNETIC ORDERINGS

Since the partially occupied d shells are strongly localized at the Mn ions, a spin magnetic moment can be assigned to each manganese atom. This circumstance enables the classification of magnetic orderings by means of the orientation of the individual atomic moments on the cation sublattice of the MnO crystal.

The magnetic orderings studied here, which are depicted in Fig. 1, are the same as those investigated by Hines et al. for MnS. Besides the FM ordering, where all spins are parallel, we distinguish five antiferromagnetic orderings: for the rs and zb polymorphs, the orderings AF1 and AF2 are characterized by a stacking of monolayers (with opposite spins in adjacent layers) along the [100] and [111] directions of the conventional cubic unit cell. The orderings AF3, AF4, and AF5 exhibit a bilayer stacking along the [210], [110], and [100] directions, respectively.

All considered spin arrangements can be labeled in terms of the respective numbers of spin-parallel and spin-antiparallel nearest (NN) and next-nearest neighbors (NNN) on the Mn sublattice (see Table I). In the face-centered cubic rs and zb structures as well as in the hexagonal wz geometry, where the Mn ions are hexagonal close packed, each cation is surrounded by 12 NN and 6 NNN. The terminology for the spin arrangements of the cations in the wz structure is derived from the cubic case. For the hexagonal lattice, two arrangements, AF2a and AF2b, with the same number of (anti-)parallel NN and NNN spins as within the cubic AF2 ordering are possible (cf. Fig. 1).

III. COMPUTATIONAL DETAILS

All DFT calculations have been performed using the Vienna ab initio simulation package (VASP). The Mn 3d, Mn 4s, O 2s, and O 2p electrons are considered as valence
states. The one-particle wave functions are expanded in a basis set of plane waves up to a cutoff energy of 400 eV, whereas the projector-augmented-wave method\textsuperscript{43} is applied to describe the wave functions in the core regions with an accuracy comparable to all-electron calculations.

For the description of XC, the GGA parametrization of Perdew and Wang\textsuperscript{43,44} with the interpolation for intermediate spin polarization suggested by von Barth and Hedin\textsuperscript{45} is applied. GGA+$U$ calculations are based on the scheme of Dudarev et al.,\textsuperscript{46} where only the difference between the on-site interaction and the exchange parameter, $U$–$J$, enters the energy functional. Therefore, all values for $U$ given throughout this paper are effective values representing $U$–$J$. Furthermore, we apply the hybrid functional HSE03,\textsuperscript{38,47} which comprises 1/4 nonlocal short-range Fock exchange, and can, hence, be expected to deal better with strongly localized states than DFT-GGA.

For the cubic structures, unit cells containing two (FM), four (AF1, AF2), or eight atoms (AF3, AF4, AF5) are used. The corresponding Brillouin zones (BZs) are sampled by a mesh of $10 \times 10 \times 10$ (FM), $11 \times 11 \times 7$ (AF1), $8 \times 8 \times 8$ (AF2, AF3), $12 \times 8 \times 6$ (AF4), or $12 \times 12 \times 4$ k points (AF5). The wz orderings are described within a 16-atom orthohexagonal unit cell (see, e.g., Ref. 39) and $4 \times 4 \times 4$ k points are employed in reciprocal space. The given k-point sets yield well-converged total energies with an accuracy of 1 meV/f.u. or better.

The absolute values of the total energies given throughout this paper are equivalent to the respective cohesive energies since the total energies of the spin-polarized atoms have been subtracted. For crystal structures with internal degrees of freedom, the atomic positions are relaxed until the Hellmann-Feynman forces are below 1 meV/Å. In order to determine the equilibrium volume $V_0$, the total energy $E_{\text{tot}}$, the isothermal bulk modulus $B_0$, and its pressure derivative $B'_0$, the energy versus volume curves are fitted to the Murnaghan\textsuperscript{48} equation of state.

### IV. STRUCTURAL PROPERTIES

#### A. Energetic ordering within GGA

In Table II, the total energies as well as the equilibrium volumes obtained by fitting the energy versus volume curves

### TABLE II. Deviations of the minimum total energy $\Delta E_{\text{tot}}$ (in meV) and the equilibrium volume $\Delta V_0$ (in Å$^3$) per formula unit relative to the values $E_{\text{tot}}=−9.731$ eV and $V_0=21.92$ Å$^3$ of the rs-AF2 structure within DFT-GGA.

<table>
<thead>
<tr>
<th>Ordering</th>
<th>$\Delta E_{\text{tot}}$</th>
<th>$\Delta V_0$</th>
<th>$\Delta E_{\text{tot}}$</th>
<th>$\Delta V_0$</th>
<th>$\Delta E_{\text{tot}}$</th>
<th>$\Delta V_0$</th>
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<tr>
<td>rs</td>
<td></td>
<td></td>
<td>wz</td>
<td></td>
<td>zb</td>
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<tr>
<td>AF1</td>
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<td>−0.05</td>
<td>−248</td>
<td>3.63</td>
<td>−277</td>
<td>3.55</td>
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<tr>
<td>AF2/AF2a</td>
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<td>0.00</td>
<td>−186</td>
<td>3.92</td>
<td>−177</td>
<td>4.05</td>
</tr>
<tr>
<td>AF2b</td>
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<td>−126</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>AF3</td>
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<td>−248</td>
<td>3.63</td>
<td>−284</td>
<td>3.52</td>
</tr>
<tr>
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<td>4.03</td>
<td>−188</td>
<td>3.93</td>
</tr>
<tr>
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<td>−0.23</td>
<td>107</td>
<td>5.85</td>
<td>134</td>
<td>5.86</td>
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calculated within GGA (Fig. 2) to the Murnaghan equation of State (Ref. 48) are given. The values for all magnetic orderings are given with respect to the energy and equilibrium volume of the rs-AF2 arrangement of atomic spins. In accordance with many other LSDA/GGA calculations,18,22,32,37 we find the AF2 ordering to be the energetically most favorable one within the rs structure. The stability of the rs-AF2 phase is usually explained with the aid of the concept of indirect superexchange49 between spin-antiparallel Mn2+ ions. Thereby, the exchange interaction between NNN Mn ions is mediated along the cubic axes by the occupied 2p orbitals of the O2− ions.50 By means of this model, it can be understood that the AF2 ordering is energetically favored, since it features the largest number of spin-antiparallel NNN (cf. Table I). Moreover, the AF4 ordering with four spin-antiparallel NNN per Mn ion is the second lowest in energy. Pursuing this scheme, AF3 and AF5 (with two spin-antiparallel NNN each) would follow. The AF1 and especially the FM ordering, which do not exhibit any antiparallel second-nearest neighbors, would be comparably unfavorable. However, having a look at Table II, one finds that this simple picture does not hold for the orderings higher in energy. This is due to the non-negligible NN interaction and the comparable strength of the NN and NNN coupling constants. For the calculation of these coupling constants or exchange integrals within a Heisenberg model, we refer to Sec. VI. Compared to the LSDA values given in Table I of Ref. 37, we find much lower total-energy differences between the rs magnetic orderings. However, our results are in reasonable agreement with the findings of Pask et al.,32 which were also obtained within LSDA. From Fig. 2 of Ref. 32, one obtains an energy splitting between rs-AF2 and rs-AF1 of about 45 meV, and between rs-AF2 and rs-FM of about 70 meV.

In addition, we have investigated MnO in the wz and zb crystal structures. For both tetrahedrally coordinated polymorphs, the AF3 ordering is the energetically most stable one, closely followed by the AF1 ordering. This can be attributed to the strong antiferromagnetic coupling of NN Mn atoms and will be discussed in Sec. VI in more detail. The relative energetic ordering within the wz structure is in agreement with the findings of Gopal et al.,37 except for AF2b lying above and not below AF4 and AF2a in our calculations. This discrepancy may be due to the use of the AF2b atomic geometry to compare the total energies for all spin structures in Ref. 37. Another reason might be their application of LSDA instead of GGA.

Surprisingly, the total energies of the lowest magnetic orderings in the tetrahedrally coordinated wz and zb structures are well below the energy of the rs-AF2 structure (see Table II and Fig. 3) which is in clear contradiction to experimental findings.16,51,52 Within DFT-GGA, zb-AF3 turns out to be the energetically most favorable one among the investigated crystal structures, whereas rs-AF2 seems to be a high-pressure modification. The rs equilibrium volume is about 4 Å3/f.u. smaller than the ones for the wz and zb structures while the equilibrium volumes of the latter two are very similar.

In contrast to earlier assumptions, we have to conclude that DFT-GGA clearly fails in determining the ground-state structure of MnO. Applying the LSDA instead of the GGA functional does not change the situation qualitatively. A similar observation has been made for MnN, for which DFT-GGA predicts zb-AF1 instead of rs-AF1 to be the ground state.34,35

B. Structural parameters

In Table III, the structural parameters, i.e., cohesive energies, equilibrium volumes, isothermal bulk moduli, and their pressure derivatives, are compiled for the energetically lowest magnetic ordering of each crystal structure and compared to literature values. In addition, the respective values for the local magnetic moments of the cations (without orbital contributions) are given.

For the rs and zb structures, which do not have any internal degrees of freedom, these quantities have been calculated both for the ideal crystal structures and the ones distorted due to the influence of the spin ordering. The latter were obtained by full ionic relaxation of the magnetic unit cell. In the case of rs-AF2, the magnetic ordering causes a rhombohedral distortion along the [111] direction of the cubic unit cell16,17,55 which can be quantified by an angle α corresponding to the deviation from the 90° angle between two cubic lattice vectors. Positive values of α indicate a compression of the cell. The angle α is also given in Table III. Very recent refined neutron-scattering measurements find an additional lowering of the rhombohedral symmetry and, hence, a monoclinic Bravais lattice.59 However, such extremely small geometrical changes are neglected here. In the case of the wz structure with the parameter u as internal degree of freedom, we present calculations for the ideal structure with u = 3/8 as well as for the relaxed geometry. However, we retained the hexagonal symmetry during the structural optimization. Taking the relaxation into account does not cure the problem of DFT-GGA predicting the wrong ground-state structure since the corresponding total-energy changes are in the order of 10 meV and, thus, well below the energetic differences between the three crystal structures (cf. Table III and Fig. 3).

Experimental data are only available for the naturally occurring rs phase. Concerning the cohesive energy, the lattice
constant, the bulk modulus, and the local magnetic moment, we find good agreement with experiments as well as previous LSDA/GGA calculations/see Table III/. Only the rhombohedral distortion angle is overestimated, which has been discussed before22,32 for LSDA/GGA.

C. Influence of the XC functional: Spatial nonlocality and on-site Coulomb repulsion

Now, we want to address the question whether the prediction of the wrong ground-state crystal structure is a deficiency of the semilocal approach to XC within the GGA. In contrast to covalently bonded sp semiconductors, also the strongly localized d electrons have to be treated appropriately in the case of MnO and similar compounds, which is certainly beyond the scope of the LSDA or GGA. Therefore, more sophisticated functionals have to be employed.

As a first step to treat the strong on-site interaction of the d electrons in a more adequate way, a Hubbard U is included in the GGA XC functional. Beyond the one-band case, such an orbital-dependent on-site term represents an effective screened exchange interaction, since only the spin-parallel electrons contribute to the additional potential term [see, e.g., Eq. (6) in Ref. 46]. Thus, both additional exchange and correlation effects are included in the functional.

In Fig. 4, the energetic and structural properties of MnO are shown for varying values of U. Here, we focus on the energetically most favorable magnetic orderings of each crystal structure. With increasing U, the total energy increases for all crystal structures, with the two tetrahedrally bonded structures being very close in energy. For values of $U \approx 4$ eV, the rs geometry becomes favorable in comparison with...
to both the \( zb \) and \( wz \) structures, which is in agreement with the experimental findings for ambient conditions. Furthermore, we observe an increase in the equilibrium volumes and a decrease in the bulk moduli with increasing \( U \). This can be interpreted as a reduced stiffness of the crystal due to the augmented repulsion of the \( d \) states. The local magnetic moment is enhanced by the inclusion of the on-site interaction yielding better agreement with experiment. Finally, also the rhombohedral distortion angle for the relaxed \( rs \) structure is reduced by turning on the \( U \) term in the potential, whereas the best matching with measured results is found for \( U \approx 6 \) eV.

Anisimov et al.\textsuperscript{28} and Franchini et al.\textsuperscript{30} propose \( U \approx 6.0 \) eV to obtain good agreement with measurements for the ground-state properties of the \( rs \) structure. Nevertheless, the lack of an \textit{ab initio} procedure to fix \( U \) proves to be the major drawback of the GGA+\( U \) method. In literature, several suggestions have been made\textsuperscript{28,60} but often \( U \) is considered to be a tunable parameter of the functional. In consequence, the method has little or no predictive power. Moreover, studying excited-state properties, such as densities of states (DOSs), the value of \( U \) which is most appropriate might differ from the one for the ground-state properties, since the screening of the interaction is different. Indeed, for \( rs\text{-MnO} \), we obtained the best agreement with parameter-free HSE03+\( G_{0}W_{0} \) calculations for \( U=2 \) eV, however, taking into account an additional scissors shift for the conduction bands.\textsuperscript{30,22}

In order to unravel the influence of exchange and correlation on the energetic ordering of the different crystal structures, we applied also the HF functional to calculate the structural properties of ideal \( rs\text{-MnO} \) and \( wz\text{-MnO} \). For the \( rs \) structure, we find reasonable agreement with previous calculations for the cohesive energy.\textsuperscript{53} Because of the complete neglect of correlation effects, the total energy is by far overestimated. However, the \( wz \) structure is still lower in energy than the \( rs \) structure, even though the difference is much smaller than in GGA (see Fig. 4). This suggests that the self-interaction error inherent to the GGA functional cannot be the sole or most important source of error as sometimes\textsuperscript{27} assumed in literature.

The general overestimation of electron correlation for fractionally occupied open subsystems (such as the partially filled \( d \) shells in MnO) within a semilocal treatment of XC can be reduced by utilizing a hybrid functional with partial Fock exchange.\textsuperscript{61,62} However, the HSE03 functional, which features 1/4 of nonlocal screened Fock exchange, does not solve the problem: albeit the total energy is lowered in comparison to the HFA, a slight preference of the \( wz \) structure remains.

Within the GGA+\( U \) approach, the \( U \) term can be thought of as a penalty functional which disfavors fractional occupation\textsuperscript{60} and corrects the semilocal approach in a similar way as the admixture of Fock exchange does. The inability of the HSE03 functional to predict the correct ground state has to be attributed to the neglect of correlation effects, which are beyond the ones included in the hybrid functional, but which can be described by the on-site interaction term \( U \) within the GGA+\( U \) scheme.

V. ELECTRONIC STRUCTURE

The strong influence of the atomic coordination and the magnetic ordering on the energetic order of the crystal structures is mediated by the respective electronic structures. This is illustrated in Figs. 5 and 6.

Figure 5 shows the total DOS as well as the orbital projected partial DOS (PDOS) for \( rs\text{-MnO} \) in the six considered magnetic orderings. All curves are calculated at the \( rs\text{-AF2} \) lattice constant within the GGA. For all magnetic arrangements, the uppermost valence bands and the lowest conduction bands are dominated by Mn 3\textit{d} states. Thereby, for both the filled and empty states, the \( e_{g} \)-derived bands are higher in energy than the \( t_{2g} \) bands. The occupied O 2\textit{p} levels lie below the valence \( d \) states. The CBM is formed by a Mn 4\textit{s} band.

Usually, the electronic structure and the bonding in a crystal are predominantly determined by neighboring atoms. For that reason, spin orderings with the same NN coordination, such as AF2 and AF4 or AF1 and AF3, exhibit quite similar DOS concerning the oxygen-related bands, the occupied \( t_{2g} \)
bands, and the 3$d$ conduction bands. However, there are significant differences concerning the occupied $e_g$ states. In the spin arrangements AF2 and, less pronounced, in AF4, they form a relatively sharp peak just below the VBM, while the corresponding structure is very broad in the remaining orderings. Thus, AF2 and AF4 are insulators, whereas the gap is closed in the other orderings and they prove to be metals. The energetic order of the magnetic structures in Table II is obviously related to the degree of their metallic or nonmetallic character.

According to Terakura et al.\textsuperscript{18} the width of the $e_g$ peak can be explained by the NNN interaction. Due to the strong oxygen-mediated intersublattice coupling between the conversely occupied Mn sublattices, the $e_g$ peak is lowered in energy in the AF2 ordering, whereas the intersublattice coupling is absent in AF1. Moreover, the broadness of the $e_g$ peak is due to the intrasublattice coupling which proves to be very strong in AF1 but is weak in AF2. In this context, it can be understood that AF4, with four next-nearest Mn neighbors belonging to the other sublattice, possesses still a rather pronounced $e_g$ peak. AF3 and AF5 feature only two second-nearest-neighbor Mn atoms within the other sublattice and, therefore, exhibit a quite broad occupied $e_g$ peak.

In order to address the question why different XC functionals favor different ground-state structures, we plot the DOS of ideal $rs$-AF2 and $wz$-AF3 in Fig. 6. For the $rs$ structure, GGA, GGA+U, and HSE03 yield qualitatively similar DOS. Apart from the gap, the most important difference is

FIG. 5. (Color online) DOS and PDOS of $rs$-MnO for six magnetic orderings within GGA. In the ferromagnetic case, results are depicted for the majority (minority) spin channel in the upper (lower) panel. Gray-shaded areas indicate the total DOS. Green (light gray) lines represent the PDOS of the $p$ orbitals while the PDOS of the $d$ states with $t_{2g}$ and $e_g$ symmetry are denoted by the thick and thin black lines, respectively. The valence-band maximum or the Fermi energy (for the metallic structures) is used as energy zero. Occurring band gaps are indicated by vertical black lines. All curves are convolved with a Gaussian of 0.6 eV full width at half maximum.

FIG. 6. (Color online) DOS and PDOS of MnO in (a) $rs$-AF2 and (b) $wz$-AF3 for the XC functionals GGA, GGA+U ($U = 4$ eV), HSE03, and HF. Gray-shaded areas indicate the total DOS. The PDOS of the $s$, $p$, and $d$ states is represented by blue (dark gray), green (light gray), and black lines, respectively. All calculated curves are convolved with a Gaussian of 0.6 eV full width at half maximum. The VBM or the Fermi energy (for the metallic structures) is used as energy zero. Occurring band gaps are indicated by vertical black lines. For comparison, experimental photo-emission data are shown: x-ray photoemission spectrum (dashed) from Ref. 63 and the x-ray photoemission spectrum (dashed) from Ref. 64.
the enhanced hybridization of $p$ and $d$ states for the GGA + $U$ and the HSE03 functionals. The main features of the DOS, except for the conduction-band onset, agree at least qualitatively with the measured photoemission spectra. In the HF limit, however, the DOS is completely altered due to the neglect of correlation effects. Also self-interaction corrected DOS (Ref. 27) deviate strongly from experimental findings since the valence 3$d^5$ states lie below the $p$ states in this case.

The DOS for wz-AF3 shows a distinct separation of the $p$ and $d$ valence bands with a gap larger than 1 eV in between. This separation is significantly reduced for GGA+ $U$ and HSE03 and vanishes completely in the HF case resulting in a strong hybridization of $p$ and $d$ states. A similar behavior can be observed for the rs structure. A reduction of the band-structure energy, which proves to be sensitive to the change of the crystal structure, goes along with the hybridization. This effect is slightly stronger for the rs structure and, hence, leads to a destabilization of the wz structure with respect to the rs structure.

VI. HEISENBERG MODEL

A. Coupling constants

In order to discuss the phase transition between antiferromagnetically ordered MnO in a certain crystal structure and the respective paramagnetic phase, we use the results of the ab initio total-energy calculations to fit the parameters of an effective Heisenberg model Hamiltonian,

$$H(V)=H_0(V) - \frac{1}{2} \sum_{i,j} J_{ij}(V) S_i \cdot S_j,$$

where the magnetization of the Mn$^{2+}$ ion at the lattice site $i$ is represented by the (effective) spin operator $S_i$. The nonmagnetic part of the Hamiltonian $H_0(V)$ as well as the so-called exchange parameters or coupling constants $J_{ij}(V)$ depend on the crystal volume $V$. The model is justified if all magnetic ions are well separated so that the overlap of their electronic wave functions is negligibly small. Furthermore, the symmetry $J_{ij} = J_{ji}$ should be fulfilled and no self-interaction occurs, i.e., $J_{ii} = 0$.

In the limit of a generalized Ising model, i.e., in the framework of collinear magnetism, an additional mean-field approximation (MFA) can be made and Eq. (1) reduces to

$$H_{\text{MF}}(V) = E_0(V) - \frac{1}{2} \sum_{i,j} J_{ij}(V) (S_i^z - \langle S_i^z \rangle)(S_j^z - \langle S_j^z \rangle)$$

with the expectation values of the nonmagnetic part of the Hamiltonian $E_0(V)$ and of the $z$ component of the atomic spin $(S_i^z)$. If all lattice sites are equivalent apart from the spin orientation, the sum runs over shells of equidistant neighbors,

$$H_{\text{MF}}(V) = H_0(V) - \frac{N}{2} \sum_i (z_i^0 - z_i^1) J_i(V) (2S^z - \langle S^z \rangle)(S^z).$$

The expectation value yields

$$E_{\text{tot}}(V) = E_0(V) - \frac{N}{2} \sum_i (z_i^0 - z_i^1) J_i(V) S^2$$

with the spin quantum number $S$ and the total number of sites $N$ within the considered volume.

We fit the total energies for all magnetic orderings to Eq. (4) and replace the spin quantum number by $S = \mu / (2 \mu_B)$, where $\mu$ is the local magnetic moment of the Mn$^{2+}$ ions. The values for $\mu$ are taken from the DFT calculations (see Table III and Fig. 4). Although arbitrary geometries can be treated, we stick with the ideal structures of the rs and wz symmetries to avoid any bias introduced by ionic relaxation. Furthermore, this allows a substantial reduction of the number of coupling constants that have to be taken into account due to symmetry reasons. We restrict the sum over $i$ to the shells...
TABLE IV. Nearest- and next-nearest-neighbor exchange coupling constants \( J_1 \) and \( J_2 \) for the \( rs \) structure as well as the resulting Néel temperatures \( T_N \) and Curie-Weiss constants \( \Theta \) for the \( rs \)-AF2 ordering. Available other calculated and experimental values are listed. To facilitate comparison with the results from literature, we also give values for the coupling constants obtained for \( S=5/2 \).

<table>
<thead>
<tr>
<th>( S )</th>
<th>( J_1 ) ( \mu/2\mu_B )</th>
<th>( J_2 ) ( \mu/2\mu_B )</th>
<th>( T_N ) (K)</th>
<th>( \Theta ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>-1.7</td>
<td>-1.3</td>
<td>-3.3</td>
<td>-2.4</td>
</tr>
<tr>
<td>GGA+( U^a )</td>
<td>-1.2</td>
<td>-1.0</td>
<td>-1.2</td>
<td>-1.0</td>
</tr>
<tr>
<td>HSE03</td>
<td>-1.4</td>
<td>-1.2</td>
<td>-1.3</td>
<td>-1.1</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
<td>-0.86</td>
<td>-0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.73</td>
<td>-0.83</td>
</tr>
<tr>
<td>Other calculations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSDA</td>
<td>-2.61</td>
<td>-2.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGA</td>
<td>-1.62</td>
<td>-1.52</td>
<td>-1.62</td>
<td>-1.52</td>
</tr>
<tr>
<td>GGA+( U )</td>
<td>-0.71</td>
<td>-0.84</td>
<td>-0.71</td>
<td>-0.84</td>
</tr>
<tr>
<td>PBE0</td>
<td>-0.99</td>
<td>-0.73</td>
<td>-0.99</td>
<td>-0.73</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-0.84</td>
<td>-0.23</td>
<td>-0.84</td>
<td>-0.23</td>
</tr>
<tr>
<td>HF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^aU=4 \) eV.
\( ^b \)From magnetic susceptibilities. Reference 66.
\( ^c \)From heat capacities. Reference 68.
\( ^d \)From magnon spectra. Reference 67.
\( ^e \)From susceptibilities. Reference 69.
\( ^f \)Reference 70.
\( ^g \)Reference 71.
\( ^h \)Reference 32.
\( ^i \)Reference 37.
\( ^j \)Reference 30.
\( ^k \)Reference 72.
\( ^l \)Tight-binding (TB) theory. Reference 73.

of nearest \((l=1)\) and next-nearest \((l=2)\) neighbor cations (see Table I) since they yield the most important contributions.

The volume dependence of the coupling constants resulting from the fit according to Eq. (4) using GGA total energies is visualized in Fig. 7. Since the behavior for \( wz \) and \( zb \) is very similar, we present only results for the \( wz \) structure here. The coupling constants, which have been derived from the total-energy calculations employing various XC functionals, are shown in Fig. 8 and listed in Tables IV and V. They are computed at the equilibrium volumes of the \( rs \)-AF2 or \( wz \)-AF3 structures, respectively.

Within the GGA, the negative signs of \( J_1 \) and \( J_2 \) for the \( rs \) structure are in agreement with the fact that MnO is antiferromagnetically ordered in the ground state. At the equilibrium volume of the \( rs \)-AF2 ordering, we obtain \( J_1=-1.7 \) meV and \( J_2=-3.3 \) meV for the coupling constants. Gopal et al.\(^{37}\) find values of \( J_1=-38 \) meV and \( J_2=-58 \) meV assuming that \( S=1 \). Even scaling their coupling constants to meet \( S=5/2 \) yields values that are one magnitude larger than our results, which agree with previous findings (see Table IV). A possible reason might be that the LSDA total-energy differences between the magnetic orderings of the \( rs \) structure, which are computed by Gopal et al.,\(^{37}\) are one order of magnitude larger. Together with the correct order of magnitude for the coupling constants, our values seem to be more reliable.

Measurements yield \( J_1=-0.86 \) meV \((-0.73 \pm 0.03 \) meV\) and \( J_2=-0.95 \) meV \((-0.83 \pm 0.06 \) meV\) estimated from magnetic susceptibilities\(^{66}\) (magnon spectra\(^{67}\)) (cf. Table IV). The disagreement between our computed and the measured values may, once more, be considered as an indication for the need of an improved treatment of electron correlation. Applying the HSE03 functional, we find an overestimation of the absolute values of the coupling constants, while they are by far underestimated in the HFA, where \( J_1 \) even changes its sign. Using the GGA+\( U \) approach instead, the coupling constants approach the experimental values with increasing \( U \) (see Fig. 8). For \( U=4 \) eV, the computed \( |J_1| \) and \( |J_2| \) slightly overestimate the measured values but the relation \( |J_1| \leq |J_2| \) found experimentally\(^{66,67}\) is still fulfilled. For \( U=5 \) eV, the absolute values agree better with experiment but \( |J_1| > |J_2| \). From Fig. 7(a) and Table IV, one may...
TABLE V. Nearest- and next-nearest-neighbor exchange coupling constants \( J_1 \) and \( J_2 \) for the \( wz \) structure as well as the resulting Néel temperatures \( T_N \) and Curie-Weiss constants \( \Theta \) for the \( wz \)-AF3 ordering. Available other calculated values are listed. To facilitate comparison with the results from literature, we also give values for the coupling constants obtained for \( S=\frac{5}{2} \).

<table>
<thead>
<tr>
<th>( S )</th>
<th>( J_1 ) (meV) ( \mu/2\mu_B ) 5/2</th>
<th>( J_2 ) (meV) ( \mu/2\mu_B ) 5/2</th>
<th>( T_N ) (K)</th>
<th>( \Theta ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>12.3</td>
<td>8.3</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>GGA+( U )^a</td>
<td>4.3</td>
<td>3.5</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>HSE03</td>
<td>-5.3</td>
<td>-4.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Other calculations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSDA</td>
<td>-7.9^b</td>
<td>0.2</td>
<td>0.2</td>
<td>500</td>
</tr>
</tbody>
</table>

^a\( U=4...5 \) eV.

^bDerived from Ref. 37. The value has been averaged over the in-plane and out-of-plane coupling constants and scaled appropriately to meet the assumption \( S=\frac{5}{2} \).

conclude that GGA+\( U \) with a \( U=4...5 \) eV leads to magnetic interactions close to those derived from measurements. However, the inequality \( |J_1| \leq |J_2| \) asks for a \( U \) parameter closer to 4 eV.

The situation is somewhat different for the \( wz \) structure. Here, the NN coupling is antiferromagnetic with anomalously large values of \( |J_1| \) within DFT-GGA, whereas the NNN coupling tends to ferromagnetic ordering, but is vanishingly small (cf. Fig. 7). Thus, in contrast to the \( rs \) structure, the NN interaction is dominating. The anomalous strength of the \( J_1 \) constant within GGA might give a hint, why the \( wz \) crystal structure is erroneously favored in total-energy calculations. Applying the GGA+\( U \) functional with \( U=4...6 \) eV, the coupling strength is reduced by one order of magnitude [see Fig. 9(b)]. Taking only NN interaction into account, Gopal et al.\(^{37}\) find -23 and -28 meV for the in-plane and out-of-plane components of \( J_1 \). Bearing in mind that they use \( S=1 \) in their Heisenberg Hamiltonian, this is in agreement with our calculations.

FIG. 9. (Color online) Néel temperature \( T_N \) (black) and Curie-Weiss constant \( -\Theta \) (red, gray) at the equilibrium volumes of the (a) \( rs \)-AF2 and (b) \( wz \)-AF3 structures within GGA+\( U \). For comparison, the constants have also been calculated using the HSE03 (squares) and HF (diamonds) functionals. The shaded areas indicate the ranges of measured values for the Néel temperature (Refs. 66 and 67) (light gray) and the Curie-Weiss constant (Refs. 66, 69, and 74) (dark gray) of \( rs \)-MnO.

B. Critical temperatures

Critical temperatures \( T_{cr} \) for the transition from an antiferromagnetic or ferromagnetic phase into the paramagnetic phase can be obtained from the temperature-dependent magnetization. Within the mean-field approach, Eq. (4), one finds the expression\(^{75}\)

\[
T_{cr} = \frac{S(S+1)}{3k_B} \sum_{l=1,2} (z_l^1 - z_l^1) J_l
= \frac{2}{3} N k_B \left( E_0 - E_{fo} \right).
\]

In the ferromagnetic (antiferromagnetic) case, \( T_{cr} \) is the Curie (Néel) temperature \( T_C(T_N) \). In addition, the Curie-Weiss temperature \( \Theta \) to describe the high-temperature behavior of the paramagnetic susceptibility \( \chi_p(T)=C/(T-\Theta) \) with the Curie constant \( C \) follows as

\[
\Theta = \frac{S(S+1)}{3k_B} \sum_{l=1,2} (z_l^1 + z_l^1) J_l.
\]

Since only the total number of atoms in each neighbor shell, \( z_l^1 + z_l^1 \), enters expression (6), \( \Theta \) is entirely the same for all magnetic orderings of a given crystal structure. Moreover, \( \Theta \) is equal to \( T_C \) for the ferromagnetic arrangement.

In Fig. 9, the critical temperatures and Curie-Weiss temperatures for \( rs \)-AF2 and \( wz \)-AF3, which are derived from the coupling constants at the equilibrium volumes according to Eqs. (5) and (6), are shown for different XC functionals. The results are compared to previous calculations as well as experiments in Tables IV and V. Within GGA, the resulting temperature constants for \( rs \)-AF2 are by far too large in comparison to measured values, whereas the hybrid functional HSE03 leads to temperatures somewhat above the experimental ones. Applying the GGA+\( U \) approach, the agreement with experimental findings is quite good if the on-site Coulomb repulsion approaches a value of \( U=4...6 \) eV. However, critical temperatures derived in the MFA from a Heisenberg model are generally overestimated.\(^{75}\)
VII. SUMMARY AND CONCLUSIONS

The ground-state properties of MnO, a prototypical transition-metal monoxide with a partially filled 3d shell, have been studied in the rs, wz, and zb crystal structures. Thereby, six different magnetic orderings have been investigated in each case. Applying the GGA to exchange and correlation, the experimentally observed ordering rs-AF2 proves to be the energetically most favorable one within the rs structure. However, the zb and wz geometries turn out to be lower in energy. This contradiction to experimental findings can be overcome by using the GGA+U method with $U \geq 4$ eV instead. Also describing exchange and correlation by means of the hybrid functional HSE03 does not yield the correct ground state, although the energetic difference between the sixfold- and fourfold-coordinated crystal structures becomes smaller. Therefore, one can conclude that a description of correlation effects which goes beyond the screened exchange included in the HSE03 functional is necessary to obtain the correct ground-state structure of MnO.

The energetic and magnetic properties have been shown to be closely related to the electronic structure. The total energies of the studied magnetic orderings have been fit to a Heisenberg model Hamiltonian to derive the exchange coupling constants for the NN and NNN. Within the GGA+U treatment, we find reasonable agreement with experimental values, while the coupling constants and the deduced critical temperature for the magnetic phase transition are overestimated by far when the GGA is used.

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