

***Ab initio* study of MF_2 ($M = \text{Mn, Fe, Co, Ni}$) rutile-type compounds using the periodic unrestricted Hartree-Fock approach**

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The *ab initio* periodic unrestricted Hartree-Fock method has been applied in the investigation of the ground-state structural, electronic, and magnetic properties of the rutile-type compounds MF_2 ($M = \text{Mn, Fe, Co, and Ni}$). All electron Gaussian basis sets have been used. The systems turn out to be large band-gap antiferromagnetic insulators; the optimized geometrical parameters are in good agreement with experiment. The calculated most stable electronic state shows an antiferromagnetic order in agreement with that resulting from neutron scattering experiments. The magnetic coupling constants between nearest-neighbor magnetic ions along the [001], [111], and [100] (or [010]) directions have been calculated using several *supercells*. The resulting *ab initio* magnetic coupling constants are reasonably satisfactory when compared with available experimental data. The importance of the Jahn-Teller effect in FeF_2 and CoF_2 is also discussed.

I. INTRODUCTION

Several transition-metal (TM) oxides and fluorides crystallize in the rutile-type structure, which is the simplest and most common MX_2 structure, where each M atom is octahedrally coordinated by the X ligands. Slight distortions of the MF_6 structural units are present due to electrostatic and/or Jahn-Teller effects. The physical properties of the TM compounds with rutile-type structure vary considerably: from ionic or covalent insulators to metals, from diamagnetic to strong ferromagnetic or antiferromagnetic semimetallic or insulating systems. This feature is a challenge to modern theoretical methods. In this context a series of compounds whose physical properties exhibits a smooth variation from one member to the other provide a suitable test of theory. This is precisely the case of the MF_2 ($M = \text{Mn, Fe, Co, and Ni}$) family of ionic compounds in which the interplay between structural parameters, chemical bonding, and magnetic coupling may be expected to display such a smooth variation.

Two different *ab initio* periodic approaches are commonly used in solid-state physics to study TM compounds: the Hartree-Fock,^{1,2} and the density-functional (in its local or gradient corrected variants³) schemes. In the latter both the exchange and correlation parts of the electron-electron interaction are taken into account in an approximate way. In the former the electron exchange part is treated exactly while electron correlation is neglected. When the spin-unrestricted form of the Hartree-Fock approach (UHF) is used in the study of insulating magnetic systems, the correct sign and a reasonably good description of the magnitude of the magnetic coupling constants usually results. The *ab initio* UHF periodic approach, as implemented in the CRYSTAL98 code,^{2,4} is the method chosen in the present work. This approach has previously been applied to several large gap TM oxides [NiO , MnO ,⁵ Fe_2O_3 ,⁶ Cr_2O_3 ,⁷ La_2NiO_4 , La_2CuO_4 (Ref. 8)]

and fluorides [FeF_2 ,⁹ KCuF_3 ,¹⁰ KNiF_3 ,¹¹ K_2NiF_4 ,¹² KMnF_3 , KFeF_8 , KCoF_3 ,¹³ CuF_2 (Ref. 14)] and a qualitatively correct description of the insulating ground state and properties of the systems is attained: the optimized structural parameters and theoretical values for properties such as the formation energy, elastic constants, and magnetic coupling constants are in reasonable agreement with the experimental values. Most of those systems have been also studied by means of density-functional (DF) theory, based on the local-density approximation (LDA) or gradient corrected approaches.¹⁵⁻¹⁸ However, most of them are incorrectly described as metals at experimental geometry, or exhibiting a very small insulating gap in the most favorable cases, or in some cases giving an inverted relative stability of the magnetic phases with respect to the experiment.

Previous theoretical work on electronic structure of the rutile compounds considered in the present work are the LDA and generalized gradient approximation (GGA) approaches of Duffek *et al.*^{16,17} on several TM rutile-type oxides and fluorides, and the periodic UHF study of Valerio *et al.*⁹ on FeF_2 . The present work has two basic aims: firstly to extend the *ab initio* UHF periodic approach to the MF_2 ($M = \text{Mn, Fe, Co, and Ni}$) series of compounds to investigate possible trends in chemical bonding, magnetic coupling, and structure stability; secondly to report accurate total energies per unit cell for the compounds, which enables a discussion of the relative stability of some relevant structural and magnetic phases.

The work is organized as follows. In the following section a review of the crystal structures of the MF_2 compounds is provided. Here, the idealized structure corresponding to perfect octahedra is also introduced, in order to investigate the absolute and relative importance of the Jahn-Teller and electrostatic effects responsible for the distortions. Section III gives computational details while the results are discussed in Sec. IV: the general electronic and structural properties are

TABLE I. Calculated and experimental (in parentheses) structural parameters of the MF_2 rutile compounds, a and c are the lattice parameters (in Å), x is the fractional coordinate of the anion. The cell volume (in Å³) and octahedral interatomic distances and angles (in degrees) are also given. The energies of the ferromagnetic state using the optimized cell parameters are $-1348.927\,008$, $-1461.504\,351$, $-1580.434\,075$, and $-1705.892\,292$ hartrees per formula unit for MnF_2 , FeF_2 , CoF_2 , and NiF_2 , respectively.

| System | a | c | x | $M\text{-F}_{eq}$ | $M\text{-F}_{ap}$ | $F_{eq}\text{-}\hat{M}\text{-F}_{eq}$ | V |
|----------------|---------|---------|----------|-------------------|-------------------|---------------------------------------|---------|
| MnF_2 | 4.960 | 3.380 | 0.3050 | 2.174 | 2.139 | 77.97 | 83.15 |
| | (4.874) | (3.310) | (0.3049) | (2.132) | (2.101) | (78.16) | (78.62) |
| FeF_2 | 4.814 | 3.339 | 0.3014 | 2.148 | 2.052 | 78.01 | 77.38 |
| | (4.700) | (3.310) | (0.3013) | (2.117) | (2.003) | (77.18) | (73.12) |
| CoF_2 | 4.811 | 3.256 | 0.3051 | 2.100 | 2.076 | 78.32 | 75.35 |
| | (4.695) | (3.182) | (0.3034) | (2.058) | (2.014) | (78.75) | (70.15) |
| NiF_2 | 4.742 | 3.161 | 0.3040 | 2.056 | 2.039 | 79.50 | 71.08 |
| | (4.650) | (3.084) | (0.3037) | (2.011) | (1.998) | (79.78) | (66.68) |

presented in Secs. IV A and IV B, while Sec. IV C is devoted to the discussion of the magnetic properties. In Sec. V we present our conclusions.

II. CRYSTAL STRUCTURES AND PROPERTIES

The MnF_2 , FeF_2 , CoF_2 , and NiF_2 compounds crystallize in the tetragonal rutile structure (space group $P4_2/mnm$ or D_{4h}^{14}), characterized by three parameters: the cell edges (a and c) and the internal coordinate of the anion. The metal atoms are located at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the anions are at $(1 \pm x, 1 \pm x, 0)$ and $(\frac{1}{2} \pm x, \frac{1}{2} \mp x, \frac{1}{2})$. The experimental cell parameters have been taken from Ref. 19 (Mn), Ref. 20 (Fe), and Ref. 21 (Co and Ni), and are collected in Table I, with the corresponding UHF optimized data. The tetragonal unit cell, containing two formula units, is shown in Fig. 1. The structure consists of slightly distorted octahedra with four basal and two apical F ions. The principal axis of the octahedron at the unit-cell center is rotated by 90° with respect to those centered on the TM ions at the cell corners. The F ions are threefold coordinated, as shown in Fig. 1; one of the F- M

bonds is apical; the other two are equatorial. The magnetic paths $M1\text{-F-M}2$ and $M1$ (or $M2$)- $\text{F-M}3$ are also evident in Fig. 1; the corresponding superexchange magnetic constants will be indicated as J_1 and J_2 , respectively. A third path will be considered in the following, connecting directly two M ions in the basal plane of the unit cell; the corresponding constant will be indicated as J_3 . Magnetic interactions at longer distances were not taken into account, as they are expected to be extremely small.

MnF_2 , FeF_2 , CoF_2 , and NiF_2 are antiferromagnetic ionic insulators at low temperature; Néel temperatures are 67.4, 78.4, 37.7, and 73.2 K, respectively.^{22,23} The M atom at the cell center has opposite spin with respect to the corner M atoms (see Fig. 1). The magnetic behavior of these systems, as resulting from the literature, is the following: MnF_2 is described as an $S = \frac{5}{2}$ three-dimensional Heisenberg system with the magnetic moments parallel to the c direction.²² FeF_2 is described as a three-dimensional Ising system, with a $3.75\mu_B$ moment parallel to the c axis.^{23,25} In CoF_2 orbital and spin degeneracy and spin-orbit coupling are supposed to give rise to a $S = \frac{1}{2}$ ground state.^{22,24} The system is then consid-

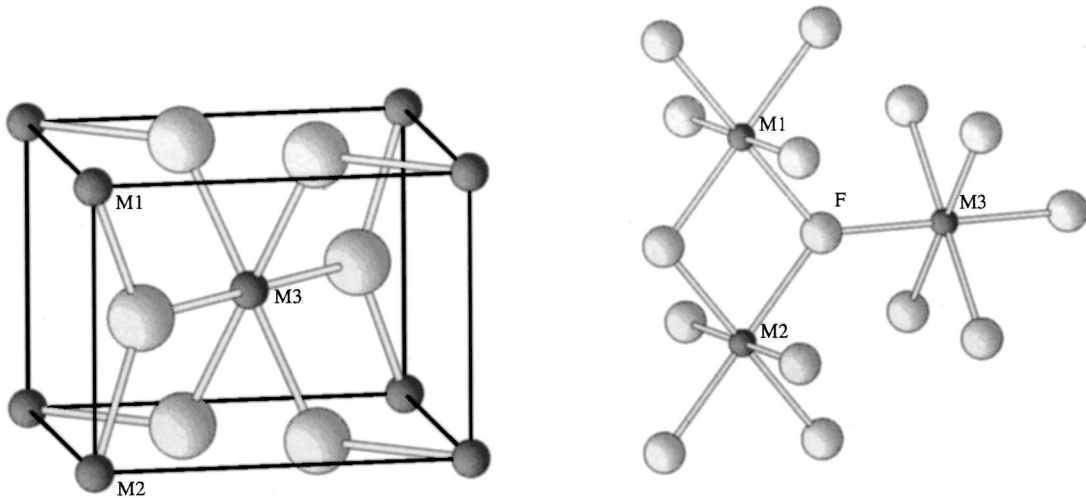


FIG. 1. The tetragonal unit cell (left) and anion coordination (right) of the rutile-type MF_2 compounds. Small spheres represent the transition metal ions. $M1\text{-F}$ and $M2\text{-F}$ are equatorial bonds of the distorted octahedra, whereas $M3\text{-F}$ is an apical bond. The path $M1\text{-F-M}2$ is then different from the $M1\text{-F-M}3$ or $M2\text{-F-M}3$ ones, and the corresponding magnetic coupling constants will be indicated as J_1 and J_2 , respectively. The third magnetic interaction considered here couples two transition-metal atoms of the basal plane of the unit cell along the $[100]$ or $[010]$ directions.

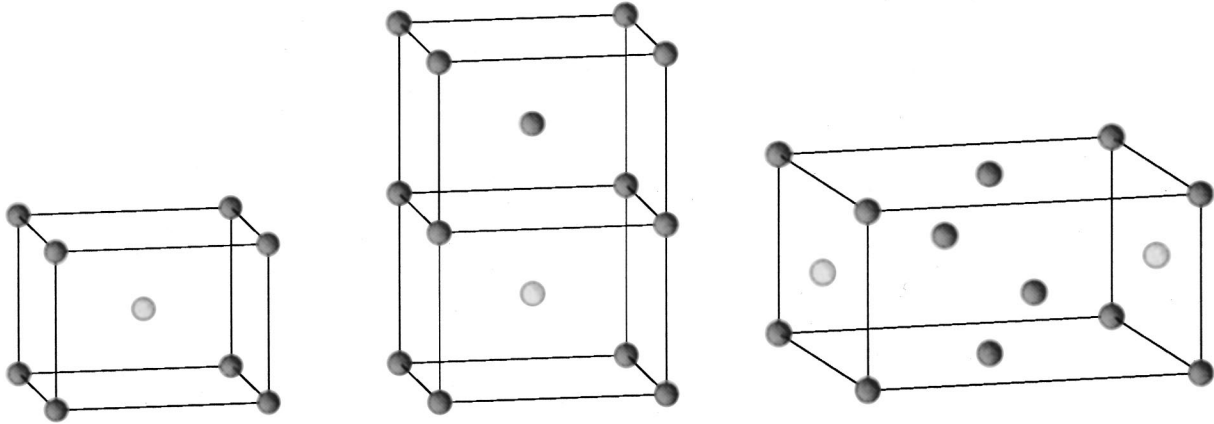


FIG. 2. The three magnetic cells that have been used for obtaining the J_1 , J_2 , and J_3 coupling constants. Only the transition-metal ions are shown (white and black indicate spin up and down, or vice versa). AFM is obtained from the crystallographic cell given in the previous figure by reversing the spin of the atom at the center of the magnetic cell, AFM1 by doubling AFM along the c axis (and reversing one spin), AFM2 by doubling the area of the basal plane of AFM, and setting the spins as indicated.

ered a highly anisotropic three-dimensional Ising antiferromagnet with effective $S = \frac{1}{2}$ magnetic centers. The magnetic moments are parallel to the c axis.²³ In our calculations we used a nonrelativistic electronic Hamiltonian; we are then unable to discuss the importance of spin-orbit coupling. The most stable Jahn-Teller configuration we obtained for Co^{2+} , which derives from the $t_{2g}^5 e_g^2$ undistorted octahedral configuration, can be seen as an approximation to the real ground state, and provides a qualitative insight into the chemical bonding and of the magnitude of the coupling between $S = \frac{3}{2}$ localized spins in this system.

NiF_2 has an antiferromagnetic (AFM) structure in which the magnetic moments show a small canting ($\sim 0.4^\circ$), that gives rise to a small residual magnetic moment along the b axis. The slightly canted magnetic moments lie on the a - b plane. Consequently, NiF_2 can be described by means of a three-dimensional Heisenberg spin Hamiltonian.^{23,26}

All of them exhibit two dominant interactions between magnetic nearest-neighbor centers along the $[111]$ and $[001]$ directions, corresponding to the J_2 and J_1 constants defined above. As regards the (very weak) J_3 coupling (along $[100]$ or $[010]$), it seems to be antiferromagnetic in all cases.

III. COMPUTATIONAL APPROACH

The calculations have been performed by using the periodic Hartree-Fock approximation¹ in its unrestricted or spin-polarized version⁴ (in order to account for the open-shell character of the systems), as implemented in the CRYSTAL98 code.² The crystalline orbitals are linear combinations of Bloch functions built from atomic orbitals (AO's) optimized for the crystal environment. The AO's are contracted real solid spherical-harmonic Gaussian-type functions (GTF's). Extended all-electron basis sets have been used. They can be indicated as 7-311G and 8-6-411-(41 d)G (two d shells), and contain 13 and 27 AO's in the former (F ion) and latter (M ion) case, respectively. There are then 106 AO's per unit cell. The atomic basis sets are described in Refs. 5 (Mn), 9 (Fe), 11 (Ni and F), and 13 (Co).

The values adopted for the computational parameters that control the truncation of the Coulomb and exchange series^{1,2}

(7 7 7 7 and 14) ensure the high numerical accuracy required for the evaluation of energy differences of the order of 10^{-5} hartree/formula unit, as is the case in the present study. A shrinking factor of 4 has been used to define the reciprocal net, corresponding to diagonalization of the Fock matrix at 21 points belonging to the irreducible Brillouin zone. The total-energy difference obtained by using larger sampling nets is smaller than 10^{-6} hartree/cell.

The optimization of the structures has been performed considering one primitive cell and the ferromagnetic state for each system. For the determination of the magnetic coupling parameters three different cells have been considered: the first one is the conventional cell, with six atoms. The second and the third ones are obtained by doubling the c axis, or the surface of the basal plane of the previous cell (12 atoms/cell). The antiferromagnetic phases arising from those supercells are shown in Fig. 2.

IV. RESULTS

A. Structural parameters

The crystal structure has been optimized in the $P4_2/mnm$ space-group symmetry by energy minimization of the ferromagnetic state. The equilibrium geometry is given in Table I. The calculated M -F bond distances show an homogeneous overestimation of 2–2.5% with respect to experiment, with a maximum error of 3% for the apical bond of the Co compound; the equatorial angles are well reproduced, with errors that are always smaller than 1° . The overestimation is in line with that found in previous Hartree-Fock calculations for other transition metal ionics, and is a consequence of the so-called correlation error (the electron-electron instantaneous interaction is replaced, at the HF level, by a mean interaction). One interesting structural aspect of the rutile-type compounds is the distorted nature of the *octahedra* due to electrostatic and/or Jahn-Teller effects. The former effect is the result of the equilibrium between attractive and repulsive Coulomb interactions and short-range Pauli repulsions. The latter appears when a degenerate electron configuration would take place in a regular crystal; in this case symmetry is broken to give a more stable state, and a distortion of the

TABLE II. Calculated equilibrium geometry parameters (in Å) of the MF₂ compounds when the octahedra are constrained to be regular (six equivalent distances and 90° angles). ΔE is the energy difference (in mhartree) with respect to the fully optimized structures.

| System | a | c | M -F | V | ΔE |
|------------------|-------|-------|--------|-------|------------|
| MnF ₂ | 5.224 | 3.060 | 2.164 | 83.50 | 6.914 |
| FeF ₂ | 5.115 | 2.996 | 2.119 | 78.39 | 7.396 |
| CoF ₂ | 5.042 | 2.954 | 2.089 | 75.10 | 7.662 |
| NiF ₂ | 4.948 | 2.899 | 2.050 | 70.97 | 6.892 |

structure occurs. This is the case for high spin d^6 , d^7 , or d^9 ions in an octahedral crystal field, where the ion loses its spherical or octahedral symmetry, different orbital orderings are possible,²⁷ and the distortion is a consequence of this ordering. These two effects are both present in the rutile case (whereas only the latter is active, for example, in the case of perovskites such as KFeF₃, KCoF₃, and KCuF₃) so that their relative importance is unknown. In order to have a feeling of their relative weight, we repeated the optimization of the structure by imposing the regular shape of the octahedron. This corresponds to keep the x fractional coordinate and the c/a ratio at the values $(2-\sqrt{2})/2$ and $(2-\sqrt{2})$, respectively (see, for instance, Ref. 15). Special attention has been paid to keep the same electron configuration as in the distorted structure. The results (referring to the ferromagnetic state) are reported in Table II. The M -F distance is in all cases intermediate between the equatorial and the apical one of the distorted octahedron; the distorted structure is (obviously) more stable than the regular one; the energy difference is around 7 mhartree in all cases; ΔE for the Mn and Ni compounds nearly coincide, whereas for Fe and Co it is 0.4 and 0.7 mhartree larger. The energy gain due to the Jahn-Teller effect is then only 5 to 10% of the energy gain related to the ion packing driven by electrostatic and short range repulsions.

B. Electronic structure

The four systems are very ionic; the Mulliken population analysis provides net charges (see Table III) very close to the formal ones (-1 and $+2$ for F and M , respectively). The strong ionic character is confirmed by the M -F bond population, which is extremely small. The Mulliken analysis data are very similar for the ferromagnetic (FM) and AFM solutions, apart from the obvious spin inversion in the AFM case. The nonspherical shape of the TM ions is evident from the

difference maps (shown in Fig. 3), the only exception being Mn²⁺, which is in a d^5 configuration. The other general feature resulting from Fig. 3 is the shrink (with respect to the free ions) of the ionic charge density, as a consequence of the short-range repulsion.

The population of the open d shells of the TM ions (see Table III) is very close to the formal values corresponding to pure d^5 , d^6 , d^7 , and d^8 configurations for Mn²⁺, Fe²⁺, Co²⁺, and Ni²⁺, respectively. If a local frame centered on the TM atom is defined, with the z axis pointing towards the apical F ion and the x and y axes in the equatorial plane, with the smallest possible angle with respect to the M -F bonds (it must be remembered that the F- M -F equatorial angles are around 78°), a clear picture of the population of the five d orbitals is obtained: in the MnF₂ case, the population is very close to one for the five orbitals: for NiF₂, only $d_{x^2-y^2}$ and d_{z^2} are singly occupied; for Fe²⁺ and Co²⁺, the t_{2g} manifold splits, and a β occupation very close to one is found for d_{xy} in the former case, and for d_{xz} and d_{yz} in the latter.

The progressive filling of the β d states, and the consequent modification of the shape and size of the transition-metal ion along the various directions, is well illustrated by the spin-density maps given in Fig. 4, referring to the AFM solution. A small spin polarization of the F⁻ ions, which is a consequence of the short-range repulsion among the unpaired electrons of the cation and the anion electrons, is predicted by the calculations and is also seen in Fig. 4. In the ferromagnetic case the polarization is larger (see also Table III), because the anion is surrounded by three cations whose unpaired electrons do have the same spin, and this costs the system a small amount of energy, as discussed below.

The projected density of states of the valence electrons for the AFM case is given in Fig. 5; in all cases the band gap is very large [Hartree-Fock (HF) tends to overestimate this quantity by a factor 2–3]; the structure for the four systems

TABLE III. Electron population data (in $|e|$ units) according to a Mulliken analysis. Q and q_{3d} are the net charges and the $3d$ orbital populations, respectively; N_s and n_s are the corresponding spin quantities. When not specified, numbers refer to the FM solution (AFM data are very similar) using the experimental cell parameters.

| System | Q | | q_{3d} | | N_s | | n_s |
|------------------|-------|-------|----------|------|-------|-------|-------|
| | M | F | M | M | F | M | |
| | | | | | FM | AFM | |
| MnF ₂ | +1.78 | -0.89 | 5.17 | 4.95 | 0.024 | 0.010 | 4.94 |
| FeF ₂ | +1.82 | -0.91 | 6.13 | 3.94 | 0.029 | 0.001 | 3.93 |
| CoF ₂ | +1.82 | -0.91 | 7.14 | 2.94 | 0.033 | 0.012 | 2.93 |
| NiF ₂ | +1.85 | -0.92 | 8.11 | 1.94 | 0.028 | 0.009 | 1.94 |

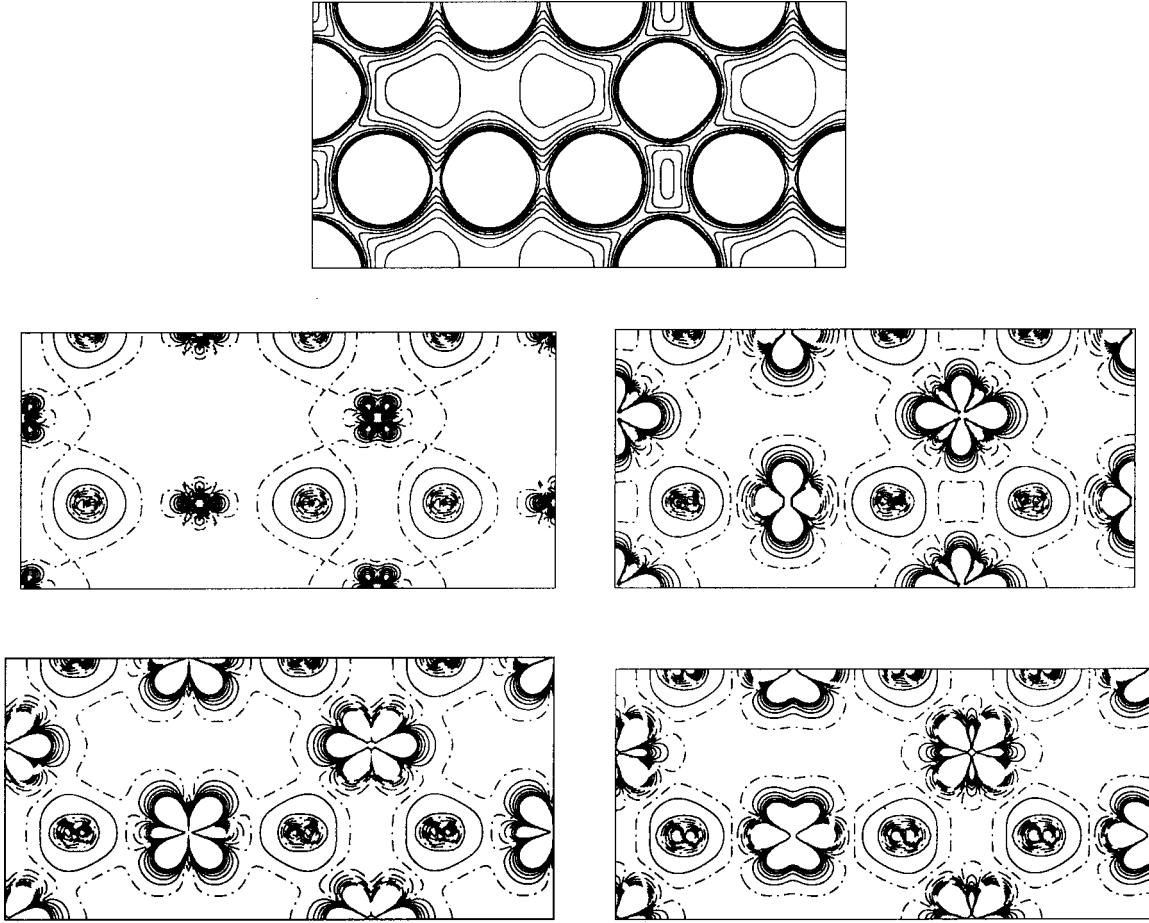


FIG. 3. Total-electron density map for FeF_2 (on top) and difference electron density maps for MnF_2 (middle left), FeF_2 (middle right), CoF_2 (bottom left), and NiF_2 projected on a (110) plane. The difference maps are obtained by subtracting, from the bulk density, the superposition of the isolated spherical-ion distributions obtained with the basis set used for the bulk. The separation between two contiguous isodensity lines is $0.01|e|a_0^{-3}$ for the total-electron density map, and $0.005|e|a_0^{-3}$ for the difference maps; the innermost curves in the atomic region correspond to $0.08|e|a_0^{-3}$ and $\pm 0.03|e|a_0^{-3}$, respectively; continuous, dashed, and dot-dashed lines correspond to positive, negative, and zero values, respectively.

is similar, with a bonding and an antibonding peak of e_g symmetry at the extremes of the band (the bottom band peak becomes higher along the Mn-Ni series) and a broad t_{2g} band in between; the anion states are spread over the whole valence band. The interesting feature is the split off of the β band in the $\text{Fe}(d_{xy})$ and $\text{Co}(d_{xz}$ and $d_{yz})$ cases; this destabilization is due to the repulsions of the electrons of opposite spin within the same shell; as a consequence of this segregation the band gap is reduced. At this point one would like to validate the picture of the electronic structure arising from periodic UHF calculations by comparison with experiment. However, the experimental data on the electronic structure of those systems are very scarce. To the best of the authors' knowledge the only available studies related to these systems are the preliminary studies of Kowalczyk *et al.*²⁸ in the 1970s and the core-level Ni $2p$ x-ray photoelectron spectroscopy (XPS) on NiF_2 of Zaanen *et al.*²⁹ Both papers deal with core-level excitations. However, these are strongly affected by final-state effects and cannot be well described by the periodic HF approach. The valence states are also discussed in Ref. 28 but the different peaks are not clearly assigned because of technical difficulties.

C. Magnetic coupling and spin density

The properties of magnetic systems are usually described by spin models to which the experimental (and calculated) data are fitted to extract their defining parameters.²² The simplest of these models, the Ising model, takes the form

$$H^{\text{Ising}} = - \sum_{\langle i,j \rangle} J_{ij} S_{z,i} S_{z,j},$$

where only the $S_{z,i}$ components of the \mathbf{S}_i magnetic moments vectors are considered and $\langle i,j \rangle$ indicates that only the interaction between nearest-neighbor magnetic moments are taken into account, as the interaction between farther neighbors is usually very small.

As the electronic monodeterminantal wave functions obtained at the UHF level are eigenfunctions of S_z , but not of S^2 , the Ising model represents the natural reference spin Hamiltonian for the mapping of the UHF energy differences in order to extract the magnetic coupling constants. However, some of the compounds studied are classified as Ising-type systems whereas others are mostly of the Heisenberg type.^{22,23,35} Since the fitting of the Hartree-Fock energies to the Ising or to the molecular field approximation to the

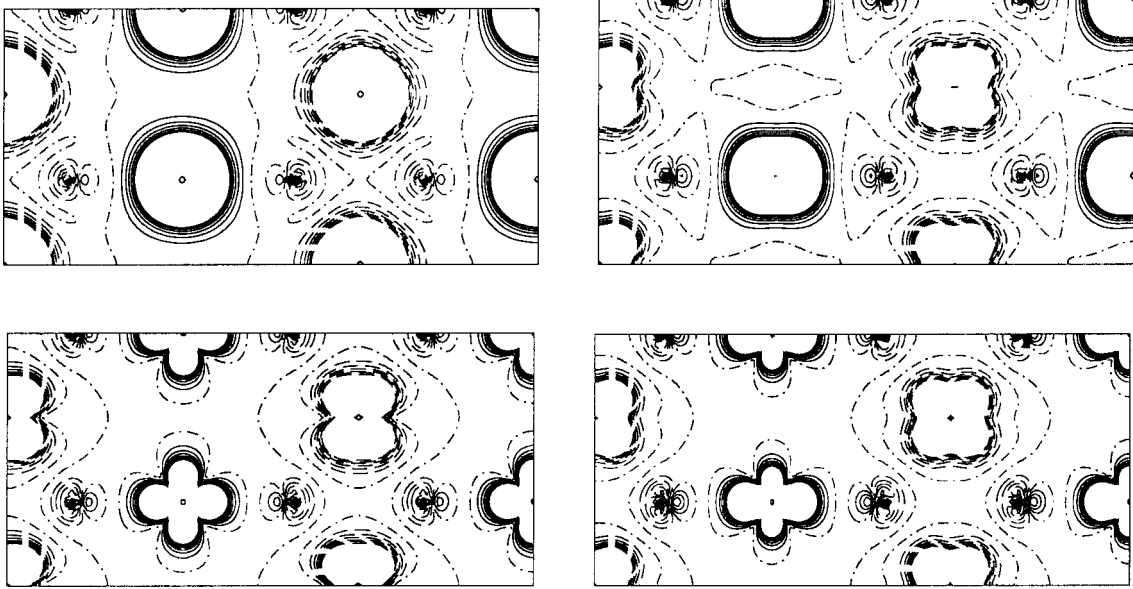


FIG. 4. Spin-density maps projected on a (110) plane of the antiferromagnetic state of MnF_2 (top left), FeF_2 (top right), CoF_2 (bottom left), and NiF_2 . The separation between two contiguous isodensity lines is $0.005|e|a_0^{-3}$; the function is truncated in the core regions at $\pm 0.03|e|a_0^{-3}$; continuous, dashed, and dot-dashed lines correspond to positive, negative, and zero values, respectively.

Heisenberg model are equivalent, the determined J_i values are valid approximations to be used in the most appropriate model (Heisenberg or Ising) for the material considered. For a recent discussion of this point see Ref. 8.

The superexchange mechanism introduced by Anderson³⁰ to explain antiferromagnetic coupling is in principle accounted for by the UHF formalism. Previous calculations with the same model (see the references in the Introduction) and recent work on cluster models at various levels of theory^{31–34} have shown that the UHF approach usually gives too small antiferromagnetic coupling constants (usually 20–30% of the experimental value; the underestimation is shown^{31,32} to be due to the small amount of electron-electron correlation included in the UHF approach), and a reasonably good description of the ferromagnetic interactions.^{11,12} From these results the periodic UHF approach is expected to give a reasonably good description of magnetic coupling in this kind of ionic solids.

As anticipated in Sec. III the three supercells shown in Fig. 2 have been considered for the calculation of the magnetic coupling parameters J_1 , J_2 , and J_3 . As the energy differences between the different magnetic states are very small, a set of consistency checks have been performed in order to verify the reliability of the obtained results as regards the numerical accuracy of the code. If in the three cells shown in Fig. 2 all the TM atoms have parallel spins, three equivalent FM states are obtained (FM, FM', FM'') that should have the same energy per formula unit, in spite of the different size and shape of the cell (and then of the different number of integrals to be evaluated, number of reciprocal space points to be used, and so on). The three energies in fact differ by less than 2 microhartrees per formula unit. In a similar way three equivalent AFM phases can be constructed (in the central cell by reversing both central spins: AFM'; in the right cell by reversing all the spins of the atoms centering the lateral faces: AFM''); also in this case the energy differences are of the order of 10^{-6} hartree per formula unit. We

can then compare different magnetic states by using unit cells of different shape and size, as the numerical noise is at least 2 orders of magnitude smaller than the physical effects we are interested in (see the ΔE values given in Table IV). The energy differences between the various magnetic phases can be related to the magnetic coupling constants J_1 , J_2 , and J_3 , along the [001], [111], and [100] (or [010]) directions, respectively, by using the Ising Hamiltonian, where only nearest-neighbor interactions between magnetic centers are included and are considered additive. For the first cell we have

$$E(\text{FM}) - E(\text{AFM}) = -16S^2J_2$$

for the cell doubled along c :

$$E(\text{FM}') - E(\text{AFM1}) = -16S^2J_2 - 4S^2J_1,$$

and for the cell with double surface of the basal plane

$$E(\text{FM}'') - E(\text{AFM2}) = -16S^2J_2 - 4S^2J_3$$

in which S^2 is the square of the spin for each TM. The theoretical results are reported in Table IV, with the available experimental magnetic coupling constants. As the total energies and energy differences given in Table IV refer to supercells containing four formula units, a factor 32 must be used in the first expression above, instead of 16.

From experiment, it turns out that all the systems (except perhaps NiF_2) exhibit an antiferromagnetic ordering, but without a clearly dominant coupling. In fact the J values are in this case much smaller than for other prototype systems.^{22,35} Moreover, the sign and magnitude of J_3 is uncertain: small and probably antiferromagnetic. For the same reasons also the calculation of the magnetic coupling constants from energy differences is difficult. The most stable calculated magnetic phase corresponds to the antiferromagnetic ordering in which the central spin moment in the unit cell is opposite to the outer spins (AFM in Fig. 2), in agree-

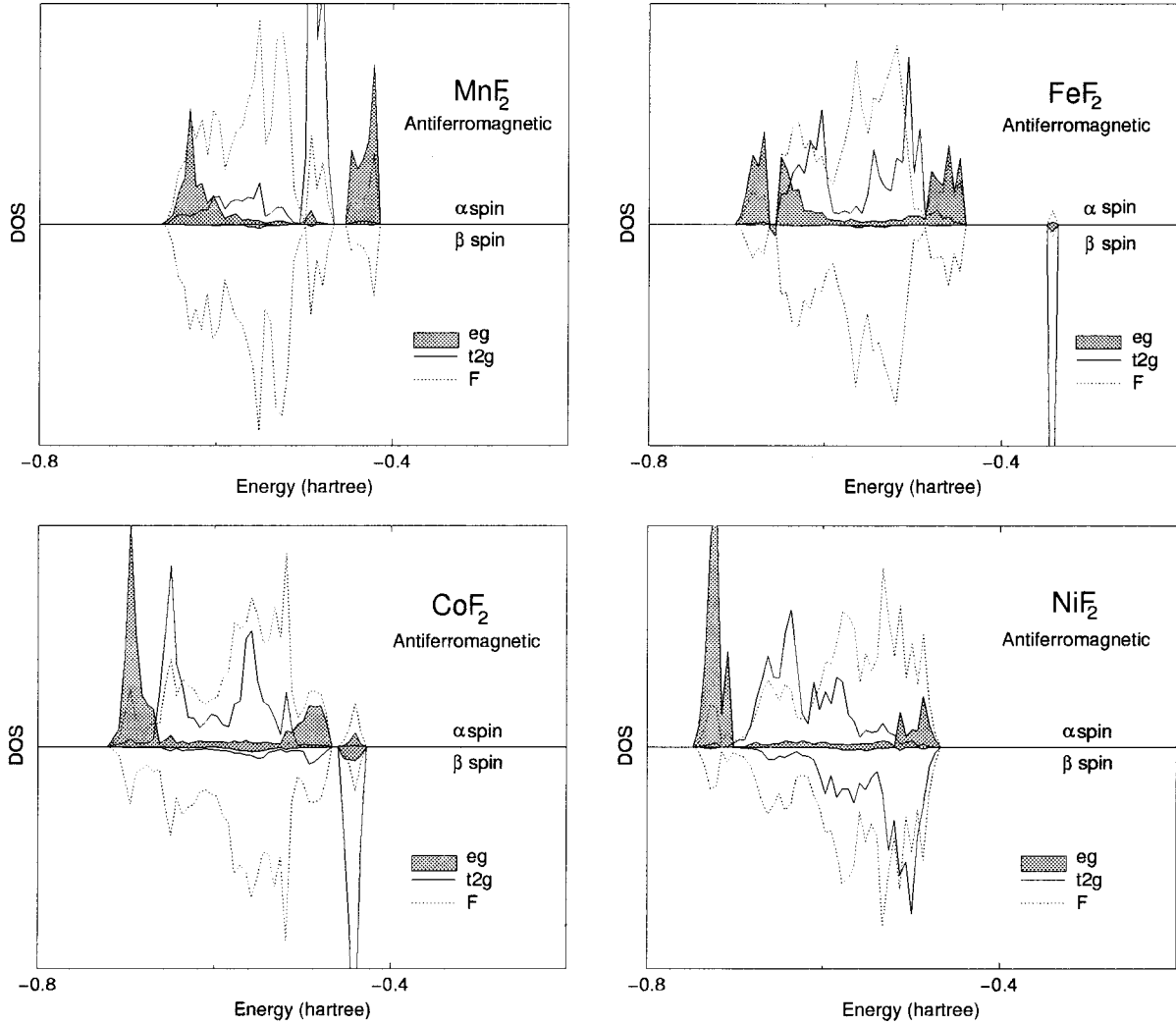


FIG. 5. Valence-projected density of states (DOS) for the antiferromagnetic phase of MnF_2 , FeF_2 , CoF_2 , and NiF_2 . Only the states of the transition metal with excess α electrons are given. The curves for the second atom are symmetric with respect to the energy axis.

ment with the experimental magnetic order determined by neutron scattering.^{22,24–26} The theoretical magnetic moments derived from the Mulliken analysis are close to the available experimental ones: $3.94\mu_B$ vs $3.75\mu_B$ for FeF_2 (Ref. 25) and 1.94 vs $1.61\mu_B$ for NiF_2 (Ref. 26). The theoretical magnetic moment for MnF_2 is $4.95\mu_B$ and $2.94\mu_B$ for CoF_2 . No ex-

perimental values have been found in the literature for those systems.

From a comparison between theory and experiment one can observe that the theoretical magnetic coupling constants J_1 and J_2 have the right sign although the ferromagnetic contribution to J is exceedingly large due to the neglect of

TABLE IV. Magnetic coupling in the MF_2 compounds: total energy (E , in hartree) of the FM state and energy differences (ΔE , in mhartree) of the AFM phases shown in Fig. 2 and used for the calculation of the magnetic coupling constants J_i (in K). J_1 , J_2 , and J_3 indicate first-, second-, and third-nearest-neighbor interactions, respectively. Experimental results are given in parentheses (see Refs. 22 and 23), E and ΔE refer to unit cells containing four formula units.

| System | E (FM) | ΔE (AFM) | ΔE (AFM1) | ΔE (AFM2) | J_1 | J_2 | J_3 |
|----------------|---------------|------------------|-------------------|-------------------|------------------|---------------------|--------------------|
| MnF_2 | -5395.707 269 | -0.540 | -0.081 | -0.272 | 2.385 (0.633) | -0.852 (-3.525) | -0.024 (-0.086) |
| FeF_2 | -5846.009 216 | -0.292 | -0.108 | -0.143 | 0.754 (0.072) | -0.721 (-5.237) | 0.041 (-0.273) |
| CoF_2 | -6321.729 353 | -0.168 | -0.082 | -0.082 | 0.076 (1.194) | -0.738 (-6.532) | 0.027 (...) |
| NiF_2 | -6823.566 664 | -0.262 | -0.072 | -0.072 | 4.649 (0.317) | -2.587 (-19.956) | 0.744 (-1.137) |

dynamical electron correlation in the UHF approach. For J_3 small ferromagnetic couplings have been obtained for all the compounds except MnF₂.

The calculated J_i values have the correct sign and, in most cases, are of the same order of magnitude as the experimental ones. Taking into account that most of the J_i are extremely small, we consider this result satisfactory. In summary, the periodic Hartree-Fock ground state for these compounds leads to a picture of the magnetic order that is in agreement with neutron-scattering measurements.

V. CONCLUSIONS

The structural, electronic, and magnetic properties of MnF₂, FeF₂, CoF₂, and NiF₂ have been investigated by using the *ab initio* periodic Hartree-Fock method in its unrestricted formulation. The calculations correctly describe the systems as antiferromagnetic insulators with strong ionic character. The optimized structural parameters are in 2–3 % in excess with respect to the experimental ones. For the Jahn-Teller ions Fe²⁺ and Co²⁺ the lifting of t_{2g} degeneracy and

stabilization has been represented appropriately. The most stable electron state corresponds to the experimentally observed AFM magnetic cell and the calculated magnetic coupling constants along the [001], [111], and [100] directions compare reasonably well with the experimental ones. The antiferromagnetic contribution to the magnetic coupling constant is underestimated at the UHF level because most of the electron correlation is disregarded. In spite of these limitations, the periodic UHF method has been shown to be able to correctly describe the magnetic order of ionic compounds and to give reasonably *ab initio* estimates for the magnetic coupling constants J_i also when the magnetic interactions are extremely small.

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