

Magnetic coupling in the weak ferromagnet CuF_2

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CuF_2 is known to be an antiferromagnetic compound with a weak ferromagnetism due to the anisotropy of its monoclinic unit cell (Dzialoshinsky-Moriya mechanism). We investigate the magnetic ordering of this compound by means of *ab initio* periodic unrestricted Hartree-Fock calculations and by cluster calculations which employ state-of-the-art configuration interaction expansions and modern density functional theory techniques. The combined use of periodic and cluster models permits us to firmly establish that the antiferromagnetic order arises from the coupling of one-dimensional subunits which themselves exhibit a very small ferromagnetic coupling between Cu neighbor cations. This magnetic order could be anticipated from the close correspondence between CuF_2 and rutile crystal structures. [S0163-1829(99)15301-3]

I. INTRODUCTION

CuF_2 is an example of a wide variety of ionic magnetic materials with a basically antiferromagnetic behavior which is slightly perturbed by a weak net ferromagnetic moment. This resulting magnetic moment is due to a Jahn-Teller distortion of the crystallographic unit cell and is commonly described as the Dzialoshinsky-Moriya¹ mechanism based on spin-orbit coupling between neighboring magnetic ions. However, this net ferromagnetism is very weak compared to the magnitude of the magnetic coupling constants within the routinely applied magnetic Anderson model.^{2,3} This model applies to situations in which the interacting spins are highly localized. Another type of magnetic interaction, not discussed in the present paper, is provided by itinerant spin waves which apply to metallic systems such as iron or nickel and which manifest completely different mechanisms of spin coupling.

The Anderson model contains the minimum physical mechanisms needed to explain antiferromagnetism. It divides magnetic interactions into direct exchange, favoring ferromagnetism, and superexchange type interactions, favoring an antiferromagnetic order. The combination of these two types of magnetic interactions in the Anderson model can be contracted to one effective exchange integral which corresponds to the magnetic coupling constant J of the well known Heisenberg Hamiltonian

$$\hat{H} = -J\hat{S}_1\hat{S}_2. \quad (1)$$

For isotropic materials the Heisenberg model can be used

to explain the temperature dependence of magnetic susceptibility or to interpret neutron diffraction experiments.⁴ We must warn that the J experimental value includes direct exchange and superexchange but also other physical mechanisms neglected in the Anderson model.^{5,6} The Anderson model is fully taken into account by considering that the magnetic interaction arises from the spin coupling of a reduced number of electrons in an orbital subspace where these active electrons are distributed in all possible ways. Therefore, the Anderson model is effectively included in a complete active space self-consistent field (CASSCF), or complete active space configuration interaction (CASCI), calculation on the appropriate spin eigenstates. However, while this approach can be used for molecular magnetic problems it cannot be applied to fully periodic systems and one must rely on the use of a broken symmetry (BS) approach.^{7,8} The BS solution is not an eigenfunction of the square of the total-spin operator S^2 and the energy differences of interest are obtained in an indirect way.⁹ The BS solution can be applied either to molecules or solids. In solid state physics this is achieved by considering ferromagnetic (F) and antiferromagnetic (AF) solutions with an unrestricted or spin polarized formalism.

Recent work has shown that the coupling constant J can be qualitatively estimated for a large variety of cubic compounds, by employing periodic unrestricted Hartree-Fock (UHF) calculations.¹⁰⁻¹³ However, these UHF calculations were able to recover only a fraction, about 30%, of the experimental magnitude of magnetic coupling constant. The difference to experiment arises from the electronic correlation effects which are not included in the BS approach.

TABLE I. Structural data for CuF_2 , taken from Ref. 27. For the interatomic distances, figures in parenthesis give the number of equivalent neighbors.

Space group	$P2_1/c$
Lattice constants	$a = 3.296 \text{ \AA}$, $b = 4.568 \text{ \AA}$, $c = 5.360 \text{ \AA}$, $\alpha = \gamma = 90.00^\circ$, $\beta = 121.15^\circ$
Positions	Cu: (0,0,0), (0, 1/2, 1/2) F: (x,y,z), (1/2+x, 1-y, 1-z) (1/2+x, 1/2+y, 1/2-z)(x, 1/2-y, 1/2+z) $x = 0.2558$, $y = 0.2968$, $z = 0.2951$,
Cu-F bond lengths	1.916 \AA (2), 1.933 \AA (2), and 2.3016 \AA (2)
Cu-Cu distances	3.296 \AA (2) and 3.5212 \AA (4)

These electronic correlation effects can be introduced by second order perturbation theory, by different configuration interaction techniques,¹⁴⁻²³ or by hybrid density functional theory (DFT).^{24,25} In the two first methods one needs to consider a local, cluster model, representation of the periodic system. The hybrid DFT methods could in principle be applied to either clusters or periodic calculations although there is not yet consistent experience for the periodic case.

The purpose of the present paper is to extend the theoretical study of magnetic coupling in systems with localized spins to the case of Jahn-Teller distorted materials. The low unit cell point symmetry of CuF_2 precludes the consideration of all possible magnetic orders from periodic calculations. Likewise, it is not possible to include the entire magnetic structure of this compound into a single cluster model. However, it is possible to circumvent these difficulties through a combined use of periodic and cluster calculations. This is precisely the main contribution of the present work. We will show that the use of cluster models allows us to verify some useful hypotheses concerning the magnetic order. These hypotheses permit us to reduce the computational problem to a magnetic unit cell which is identical to the crystallographic one.

This paper is organized as follows: In the next section we provide a short review of the crystallographic structure of CuF_2 and present a possible modelization within a fully periodic approach. This modelization rests on the hypothesis of one-dimensional ferromagnetic subunits of the three-dimensional crystal. The verification of this hypothesis is presented within a cluster model for different levels of theory, Sec. III. This allows us to approach the antiferromagnetic coupling constant within, again, a periodic UHF calculation. The last section will present our conclusions. To facilitate the physical understanding all computational details are collected in the Appendix.

II. THE CuF_2 CRYSTAL

A. Geometrical structure

The monoclinic crystal structure of CuF_2 is described by the space group $P2_1/c$ with four symmetry operators and contains two CuF_2 units per unit cell. One of the copper atoms being on the cell corner, the positions of the six atoms of the unit cell are entirely determined by the lattice parameters and the position of one fluorine atom. The experimentally determined structure parameters²⁶ have been used with-

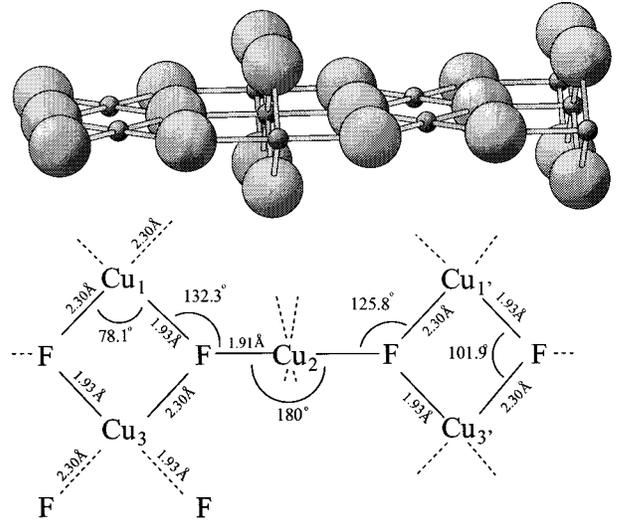


FIG. 1. Structural coordination motives of the Cu and the F ion. The coordination around symmetry equivalent Cu ions in different 1D chains, Cu_1 or Cu_3 versus Cu_2 in the projection of the structure to a plane, gives the complete octahedron. The 2D sheets, see text, go along Cu_1 to Cu_2 to Cu_3 , and should be thought orthogonal to the structure diagram in the lower part of the figure. Magnetic motives follow Cu_1 - Cu_2 - Cu_3 , or Cu_1 - Cu_3 or Cu_1 '- Cu_2 - Cu_3 directions.

out modification, and are reported in Table I. The crystal structure was determined at several temperatures and we have chosen the parameters corresponding to 77.3 K, a temperature close to the Néel temperature of 69 K.²⁷

The CuF_2 structure is commonly described as a distorted rutile structure, a structure adopted by many transition-metal oxides and halides. It is formed by octahedra of fluorine surrounding Cu cations, each fluorine anion being threefold coordinated to Cu, Fig. 1; we must point out again that all Cu atoms are equivalent and labels in this figure are introduced to facilitate the discussion. Jahn-Teller distortion of the CuF_6 octahedra has already been mentioned to be energetically favorable by breaking the ideal symmetric coordination of the copper centers. In rutile type structures, two lower-dimensional structural pictures arise, a one-dimensional and a two-dimensional periodic substructure. The first picture consists in the decomposition of the CuF_2 structure into stoichiometric one-dimensional CuF_2 chains formed by line-connected CuF_4 units, the basal planes of the coordination octahedra.²⁸⁻³¹ These one-dimensional chains follow the Cu_1 - Cu_3 line in Fig. 1. This first picture might be less pronounced in CuF_2 than in rutile itself because of the different Cu-F bond distances within the connected CuF_4 planes, 1.932 and 2.302 \AA , the latter being significantly longer than the Cu-F bond out of the plane, 1.916 \AA . The other lower dimensional picture of the three-dimensional (3D) structure emerges when linking all short distances in the crystal, Cu_1 - Cu_2 - Cu_3 , in Fig. 1, to form two-dimensional sheets or puckered layers as they are commonly denoted in the literature.²⁶ These layers, with Miller indices (100) are interconnected via the long, 2.302 \AA , Cu-F bonds and, as each of the 1D chains, each individual layer forms a neutral and stoichiometric subunit of the entire CuF_2 crystal. In the rutile structure, space group $P4_2/mnm$, these layers are also present and can be found by looking at the (101) planes of the crystal. There, F-Cu-F bond angles of 135° and 90° ap-

pear provided the idealized structure, with equal bond lengths and with all angles within one CuF_6 octahedron having 90° , is assumed. In real monoclinic CuF_2 the difference of the two angles is still present, 132.26° and 89.69° , and, as in rutile, the copper atoms linked in this manner are not the closest neighbors, which are Cu_1 and Cu_3 in Fig. 1 at a distance of 3.29 \AA , but the next neighbors, Cu_1 and Cu_2 separated by 3.55 \AA . Thus, an effective superexchange interaction via the short bridges, 1.91 and 1.93 \AA or Cu_1 - Cu_2 , in the 2D layer might dominate here over the direct-exchange term. A different balance between these two terms might be present within the 1D subunits which involves effective superexchange via the two longer, 1.93 and 2.30 \AA , Cu-F bond distances whereas the direct exchange implicates the shorter Cu_1 - Cu_3 distance. In conclusion, an analysis of the complicated geometrical crystal structure of CuF_2 suggests that magnetic order might be the result of two independent mechanisms.

B. Electronic structure

CuF_2 is an insulator, experiments show a temperature dependence of the magnetic susceptibility which clearly reveals the antiferromagnetic character of this compound. These measurements attribute a Néel temperature of 69 K to CuF_2 . Moreover, a small spin canting of 0.01° is reported, due to the geometrical anisotropy of the crystal unit cell.

To gain further insight into the electronic structure of CuF_2 , a periodic unrestricted Hartree-Fock calculation has been performed with CRYSTAL95 (Ref. 32) on a completely ferromagnetic spin arrangement. The resulting wave function shows a high ionicity with vanishing Mulliken overlap populations for Cu-F pairs and net Mulliken charges almost identical to total Mulliken charges of $+1.83$ and -0.91 on the ionic centers. Let us recall that in the Mulliken population analysis the total population at a given center is obtained by summing two terms: the net and overlap populations. The first term involves only contributions from the specified center whereas the second one includes two-center contribution through the overlap integral. Certainly, the absolute values of the Mulliken charges are affected by the choice of the basis sets and the absolute figures have a limited physical meaning. In fact, we will not argue that CuF_2 has a partial ionic character because the Mulliken charge on F centers is less than the formal charge. Instead, we insist in the fact that the shown charge partition points towards a purely ionic bonding picture. Consequently, the magnetic orbitals of the UHF solution, one band of α -spin occupation without counterpart within the β -spin orbitals, are essentially constituted by the d orbitals of the copper ions, with little contributions being attributed to the fluorine centers.

In Fig. 2 we show the density of states of the valence bands, projected onto the five basic d orbitals after rotation of the unit cell into the (011) plane. This rotation brings the previously mentioned CuF_4 plane of every second octahedron to the xy plane of the coordinate system, and permits the decomposition of the complete set of d orbitals straightforwardly. The other CuF_6 octahedron of the crystallographic unit cell is completely symmetry related to that being analyzed. The lowest-lying α -spin bands, which are well separated from the rest of the band structure, are mainly formed

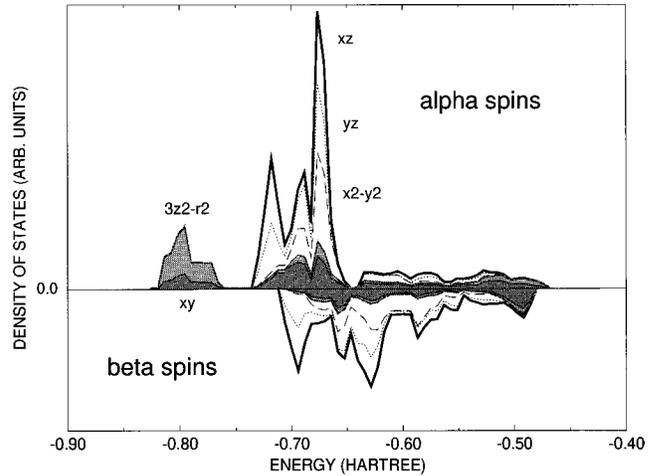


FIG. 2. Cumulative density of states (DOS) of the valence bands for the ferromagnetic structure, projected onto the Cu_1 d orbitals after rotation of the unit cell into the (011) plane. The orbitals contributing to the magnetic, only α bands, are shaded. The thick solid line gives the total d orbital contribution to the DOS. The summation of DOS is in the order xy , $3z^2-r^2$, x^2-y^2 , yz , and xz .

by the two d orbitals $3d_{3z^2-r^2}$ and d_{xy} on Cu. These α -spin bands exhibit some p character arising from the mixing to the F anions. The total Cu participation is $>85\%$ of the α electrons forming the band. The other d -orbital contributions are energetically situated within the p -band system of the anions. The participation of the $3d_{3z^2-r^2}$ and d_{xy} orbitals in the upper-lying bands reflects the distortion of the octahedron by mixing the $3d_{3z^2-r^2}$ and d_{xy} components. This is due to the asymmetric polarization brought about by the anions. The structural diagram in Fig. 1 shows the coordination of the F anion within the Cu cations along both fundamental octahedra of the unit cell. In fact, the sum of the projections of the density of states onto the copper d_{yz} , d_{xz} , and $d_{x^2-y^2}$ orbital gives vanishing contribution to the two magnetic orbitals. To close this section of results of our first set of calculations on the periodic system, we note that the mixing between the $3d_{3z^2-r^2}$ and d_{xy} orbitals in the α -spin bands is consistent with the two independent mechanisms above discussed. Without this orbital mixing only one of the magnetic coupling schemes will be possible. Finally, we report a large separation between occupied and virtual orbitals of about 0.65 a.u. for the ferromagnetic UHF solution.

C. Reasons for looking at the CuF_2 magnetic 1D coupling

The subtle equilibrium between the direct and the effective superexchange term permits access to the basic, antiferromagnetic structure of CuF_2 within a periodic ansatz. For an assumed ferromagnetic ordering within the one-dimensional chains the symmetry of the crystal is not completely destroyed and the calculations can be performed with reasonable basis sets within one crystallographic unit cell only.

Let us recall that the CuF_2 unit cell contains two copper cations belonging to two different 1D chains with the basal planes of the corresponding octahedra being nearly orthogonal to each other. Within this crystallographic unit cell any antiferromagnetic coupling consists in attributing different spins to the two copper centers. Now, two different possibili-

ties arise. The first possibility consists in attributing alternating spins within the chains, thus doubling the unit cell and completely destroying any symmetry operation for the corresponding magnetic unit cell. In the second possibility a ferromagnetic order within the chain is maintained and the system can be described by one crystallographic unit cell only, and the C_i symmetry of the system is preserved. However, this second possibility is, in principle, in contradiction to the interpretation of neutron diffraction experiments²⁶ which suggests that the magnetic unit cell, corresponding to the P_a2_1/c Shubnikov group, is the double of the crystallographic unit cell. Still, the magnitude of magnetic coupling within the chains can be effectively so small that in practice there will be no physical difference between studying the basic antiferromagnetism within the single or double crystallographic unit cell. Relying on our experience with the use of cluster models to investigate magnetic coupling, we will try to analyze the possibility of the magnetic order within the chain.

III. THE CLUSTER CALCULATIONS

A. Cluster setup

The question of ferromagnetic or antiferromagnetic ordering within the 1D chains of the 3D crystal lead us to a cluster model containing two copper atoms and two linking fluorine atoms, being oriented along the one-dimensional substructure. These four principal atoms representing the cluster center will be used as the basic unit to calculate the magnetic intrachain spin-coupling constant of the periodic system, including the long Cu-F bonds only.

When abandoning the translational symmetry of the full crystal, all symmetry operations with a finite translation vector vanish, regardless of magnetic ordering of the crystal. In the present case this means a reduction from four to only two remaining symmetry operations, leaving C_i as the resulting point group. To provide proper chemical and electrostatic surroundings to the basic cluster model, the first coordination sphere of each of the two Cu ions of the Cu_2F_2 central unit has been surrounded by fluorine centers with a less flexible basis set, leading in total to a Cu_2F_{10} quantum-chemical cluster, followed by completing the coordination-spheres of each fluorine by in total 22 total ion potentials (TIP's) with a +2 formal charge. Now this whole object is embedded in a spherical distribution of formal point charges; we assume charges of +2 and -1 for Cu and F centers, respectively. To obtain a neutral setup, shells of atom positions representing stars of ions of equal distance from the cluster were added, resulting in large oscillations of the total charge of the "point-charge sphere" with the diameter of the sphere; these oscillations are depicted in Fig. 3. Along this sphere-growing process one accidentally finds complete spheres of ions leading to a zero overall charge. A reasonable number of point charges for embedding the quantum-mechanical cluster seemed to us a total number of atom positions of 2910. This leaves us with 970 Cu sites and 1940 F sites, of which the innermost are represented by the quantum-mechanical object, the rest being the formal point charges. For a system with such low symmetry C_i and a cluster center which falls not on a site centered in the crystal unit cell the described procedure is certainly more efficient to give a well-balanced

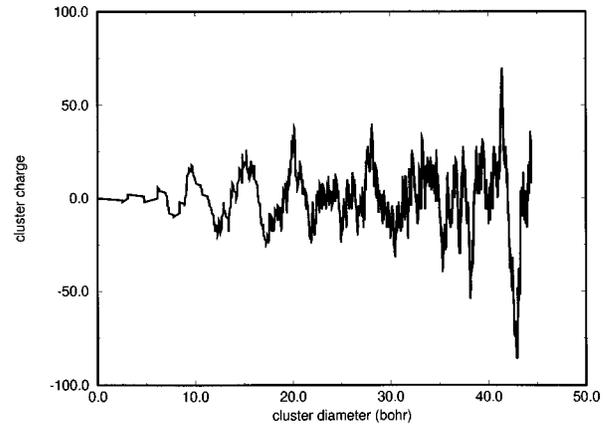


FIG. 3. Evolution of the net charge of the "point-charge sphere" around the cluster center with increasing the sphere diameter. Note that, accidentally, there exist complete spheres of ions with zero overall charge.

object with respect to the cluster center than the alternative of building a model based on the Evjen method³³ employing a unit cell with fractionary charges on the faces, vertices, and edges. The resulting electrostatic potential of our point-charge cluster, calculated at various sites within the cluster region, is in good agreement to the infinite Ewald summations. For this reason no further adaptation of the point-charge values has been applied. Finally, we would like to mention that, once the Madelung field is reasonably reproduced, the overall size of the point charge array does not affect the computed values of the magnetic coupling constant.

The triplet-coupled high-spin restricted open shell Hartree-Fock (ROHF) wave function of the Cu_2F_{10} central cluster, now in a basis set which is different from that used in the CRYSTAL calculation but with about the same flexibility, shows a good agreement to the periodic calculation. This agreement between periodic and cluster calculations is found in the Mulliken decomposition and, more important, in the composition and shape of the magnetic orbitals. Therefore, the described cluster is considered as close as possible to the full periodic structure, and we now can undertake the calculation of the intrachain coupling constant.

B. Extraction of J

For a cluster model with two magnetic Cu^{2+} ions the Heisenberg coupling constant J is simply given by the energy difference between the triplet and singlet coupled spin eigenfunctions. Therefore at all levels of theory based on the use of ab initio wave functions which lead to pure spin eigenfunctions, the magnetic coupling is given by

$$E_{|S\rangle} - E_{|T\rangle} = J. \quad (2)$$

On the other hand, one can also use an unrestricted formalism based either on a Hartree-Fock or Kohn-Sham Slater determinant. In those cases one does not have a spin eigenfunction although both determinants are eigenfunctions of \hat{S}_z , the z component of the total spin operator. This permits a connection to the Ising Hamiltonian

$$\hat{H}^{\text{Ising}} = -J \hat{S}_{z_1} \hat{S}_{z_2} \quad (3)$$

instead to the Heisenberg Hamiltonian [Eq. (1)]. In the case of two Cu^{2+} cations, the mapping from \hat{S}_z eigenfunctions onto the unrestricted determinants permits to obtain J as

$$E_{|\text{AF}\rangle} - E_{|\text{F}\rangle} = \frac{J}{2}, \quad (4)$$

where $|\text{F}\rangle$ is the high spin, ferromagnetic solution and $|\text{AF}\rangle$ is the low spin, antiferromagnetic, broken symmetry wave function. A similar relationship to Eq. (4) was earlier derived by Noodleman⁷ and Noodleman and Davidson⁸ to deal with magnetic coupling in transition metal binuclear complexes. In the case of using a DFT approach one may wonder whether one should use Eq. (4) or assume that the DFT energy associated to the broken symmetry solution corresponds to the singlet. While some authors³⁴ claim that Eq. (4) does not apply to DFT, based solely on the argument that DFT does not deal with spin eigenfunctions and does only require a density, other authors^{9,24,25} find more reasonable to stick to Eq. (4) because of the mapping to the Ising Hamiltonian and because, in the present clusters, the expectation value of \hat{S}^2 is close to 1.0, midway between singlet, $S(S+1)=0$, and triplet, $S(S+1)=2$, and consistent with Eq. (4). For other cations with total spin $S \neq \frac{1}{2}$, the equivalent to Eq. (4) is easily deduced from the mapping arguments.

To allow comparison with periodic calculation let us return to the Ising model but assuming that instead of two interacting cations one needs to deal with an infinite solid. If we assume additivity of the two-body interactions, and that each cation is interacting with z neighbors instead of one, Eq. (4) becomes

$$E_{|\text{AF}\rangle} - E_{|\text{F}\rangle} = \frac{zJ}{2}. \quad (5)$$

C. Numerical results from the cluster calculations

In order to apply the above discussed theoretical approaches to the computation of J we performed configuration interaction (CI) and broken symmetry (BS) UHF and DFT calculations. In all cases, a very small coupling constant has been obtained, nearly at the limit of the numerical accuracy of the used procedure. Nevertheless, all results show a positive sign of the coupling constant thus leading to a ferromagnetic coupling within the chosen subunit of the three-dimensional crystal. This is found for the CASCI calculations, containing the basic Anderson model and for sophisticated difference dedicated configuration interaction calculations including excitations out of the CAS with two, DDCI2, or three, DDCI3, degrees of freedom.^{35,36} At the CASCI level a very weak ferromagnetic coupling of 0.9 K is predicted (1 Hartree=315773.21 K). State-of-the-art inclusion of electronic correlation by means of either DDCI2 or DDCI3 substantially modify the calculated J but its value remains very small, 1.3 and 2.8 K, respectively. Hence, the inclusion of up to 10^6 Slater determinants does not significantly enhance the magnetic coupling within this 1D subunit. On the other hand, we would like to draw the attention to the results from the unrestricted calculations. The UHF predicts

a J of 1.9 K [Eq. (4) is used], close to the CAS value which contains the corresponding physical mechanisms. The use of hybrid exchange correlation functionals, the well known B3LYP (Ref. 37) and the BFLYP,^{24,25} which contains 50% of the Fock and Becke88 exchange functional,³⁸ predict a ferromagnetic J of 12.8 and 9.0 K, respectively.

The conclusion of this subsection is quite straightforward, namely there is a near zero magnetic coupling within the 1D subunit with a slight tendency to positive values. Adding sophisticated correlation treatments does not significantly change this picture.

D. 1D periodic calculation on the bare CuF_2 chain corresponding to the cluster model

In order to further prove that the basic physical mechanism described above is inherent to the crystal partition, we could attempt a one-dimensional periodic UHF calculation on one CuF_2 chain only. However, we must point out that this model does not include the full coordination spheres of the ions on the chain and, secondly, a proper Madelung field is lacking. Nevertheless, we obtain a weakly ferromagnetic substructure, of the same order of magnitude as in the cluster calculation. These results favor once again the posed hypothesis of a spin coupling within the chains which is, if not feeble ferromagnetic, without major importance to the overall magnetic structure. Using Eq. (5) and $z=2$ this crude periodic model predicts a J value of 9.5 K.

We have exactly the same orbitals for the ferromagnetic and the antiferromagnetic UHF solution of the system, only the coupling F bridge shows different participation, due to the two different spin signs on the Cu centers in the AFM solution. Compared to the ferromagnetic solution of the 3D periodic calculation, or to the cluster models, the $3d_{3z^2-r^2}$ orbital has here a minor importance to the magnetic structure because of the absence of a complete coordination.

IV. THE AFM 3D-PERIODIC CALCULATION

Having shown that the magnetic coupling between the closest Cu neighbors is very feeble, we can assume that the ferromagnetic coupling is, grosso modo, as favorable as an antiferromagnetic coupling. Therefore, we can now rely on the periodic calculations within a one-cell-only model. Correlation effects have been shown to be of importance even in the CuF_2 1D structure, thus we could only expect a qualitative value for the antiferromagnetic intrasheet or interchain coupling constant at the periodic UHF level. For the antiferromagnetic case of the 3D system, we have to reduce the symmetry of the crystal to C_i in order to render the two copper centers symmetry independent. To ensure that we do not deal with different symmetry-broken solutions to the Hartree-Fock equations, the ferromagnetic case has been repeated in this lower symmetry. The two copper centers in the ferromagnetic unit cell remain completely equivalent.

Likewise, for the AFM case two calculations have been performed. One of them starts from the ferromagnetic UHF density matrix, reversing every second spin, and other one takes the superposition of atomic density matrices, the default guess in CRYSTAL calculations. The two resulting AFM UHF wave functions are completely identical, however, convergence is in both cases quite slow, taking about 70 cycles

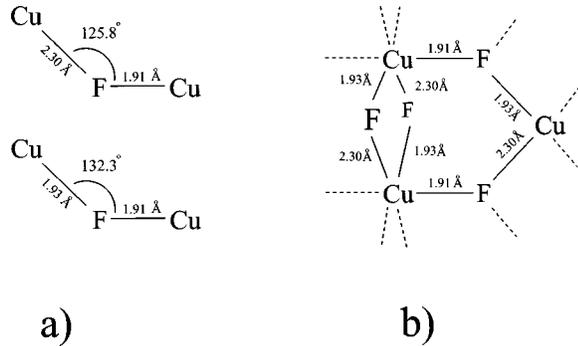


FIG. 4. Two different types of basic clusters: to obtain the complementary, antiferromagnetic spin-coupling constant to different Cu-F-Cu clusters have to be considered (a), and in order to include both spin-coupling aspects one single cluster with three magnetic centers should be used (b).

to arrive at a convergence with respect to the total energy per cell (Cu_2F_4) below a threshold of 10^{-7} .

The antiferromagnetic solution appears to be more stable than the ferromagnetic one, by 1.46497×10^{-4} hartree. From this energy difference per unit cell, two copper ions, Eq. (5) and $z=4$ we derive an effective antiferromagnetic of J of -23.2 K coupling the 1D chains. Inclusion of electron correlation usually adds a factor of 3 to CAS or UHF calculation.^{14–23} Hence, one would expect a final antiferromagnetic coupling of about 60 K, a value which is of the order of magnitude that one would expect from the experimentally observed Néel temperature of 69 K.²⁷

V. FURTHER CONSIDERATIONS

The cluster chosen represented a section of the 1D substructure only. If one attempts to compute either the interchain coupling or an effective isotropic coupling constant J , other cluster models should be considered. In the first case, this would lead to be the asymmetric $\text{Cu}_1\text{-F-Cu}_2$ (see Fig. 1) unit including the 132.26° bond angle, Fig. 4(a). In the second case the minimal cluster might be a Cu_3F_4 central unit around which the proper coordination spheres have to be built, in Fig. 4(b). The latter case demands the simultaneous coupling of three spins leading now to one quartet and two doublet states. Three different pair-coupling constants arise because of the different Cu-F bond lengths involved in the CuF_2 unit attached to the Cu_2F_2 cluster representing the 1D periodic chain. Both of the additional cluster models are non-symmetric with respect to space, even for ferromagnetic spin settings. With our present implementations and means of computations, the first of these clusters is still accessible in the same way as shown for the intrachain magnetism, however, the calculations on the cluster representing both aspects of the magnetic coupling in CuF_2 , the intrachain and the intralayer interactions, is still beyond the scope of our present *ab initio* modelization.

On the other hand, additional periodic calculations might be needed to complement the cluster study. However, this would require to consider periodic calculations with the double cell and because of the complete loss of symmetry these calculations are out of the present computational capabilities. Results in the present work summarize state-of-the-

art calculations for magnetic coupling in the monoclinic CuF_2 compound within the computational facilities available and existing computer codes.

VI. GENERAL CONCLUSIONS

A cluster model provided a convenient tool to investigate details of the electronic and magnetic structure of CuF_2 revealing once again the validity of the very localized picture of the magnetic interactions. This cluster study has delivered the basis for the description of the magnetic coupling of such a complicated periodic system where many coupling schemes are, in principle, possible. Periodic calculations in a single unit cell for both ferromagnetic and antiferromagnetic orders completed the *ab initio* description of the magnetic structure of the monoclinic CuF_2 crystal. The overall picture points towards a noticeable antiferromagnetic order coupling of Cu cations within two-dimensional sheets of the crystal structure. Due to the subtle competition between direct exchange and antiferromagnetic interactions (superexchange terms plus those arising from electronic correlation effects) between the sheets, these cations are weakly ferromagnetically ordered which is, in principle, in contradiction to experiments.²⁶ The present *ab initio* study suggests, however, that strong antiferromagnetic order between the sheets can be excluded. This point has been verified by accurate cluster model calculations and is the reason why the study of the antiferromagnetism within the periodic approach has been possible within a single unit cell. Of course, the net weak ferromagnetism due to a spin-canting or Dzialoshinsky-Moriya mechanism is inaccessible with the Hamiltonians employed, which are purely nonrelativistic and exclude spin-orbit coupling terms.

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APPENDIX: COMPUTATIONAL DETAILS

All periodic calculations employ the CRYSTAL95 program package (linear combination of atom-centered Gaussian crystal orbitals), with basis sets designed and used for describing the magnetic structure of perovskites (KNiF_3 and KCuF_3).^{12,13} On Cu the basis is a 8/6411/41 contraction of Gaussian primitives for $s/sp/d$ shells, and for fluorine the contraction reads 7/411 as s and sp shells. Computational parameters for the CRYSTAL package are best described by the cutoff threshold parameters ITOL 1–5 of CRYSTAL,³² which have been chosen as 7,7,7,7, and 14, respectively. For integration in reciprocal space the k -space grid parameter has been set to a value of 6 yielding in combination with the four

symmetry operations of the ferromagnetic CuF_2 structure—space group $P2_1/c$ —a total of 80 irreducible points in the first Brillouin zone and 112 irreducible k points for the antiferromagnetic structure (P_1^-). Calculations demanded up to 100 MB of disk space when using the Direct-SCF version of CRYSTAL95, and up to 8 GB when storing all bielectronic integrals on disk. Calculations were performed on IBM workstations in Turin and on the IBM SP2 machine of CESCA in Barcelona.

To construct the central cluster and the geometrical setup of the cluster surroundings representing the active local section of the CuF_2 crystal the geometry manipulation options of CRYSTAL program were used. Having chosen the proper Cu_2F_{10} cluster and its surroundings, SCF molecular calculations were carried out employing the PSHF-CIPSI chain of programs³⁹ to obtain a multireference wave function which uses a complete active space configuration interaction (CASCI) as reference space. The CASCI wave function was constructed by using the molecular orbitals obtained from a ROHF on the triplet state. The CAS is defined by the combinations of open-shell d orbitals which lead to the singlet or triplet coupling of the two magnetic Cu^{2+} centers. For the cluster calculations three different types of basis sets have been considered: for Cu cations a large core pseudopotential with a $2/2/2$ ($s/p/d$) contracted basis set of Hay and Wadt,⁴⁰ for F anions forming the bridge of the central Cu_2F_2 unit, an

all electron basis with a $4/3/2$ contraction scheme, and for the F anions directly coordinated to the Cu ions a pseudopotential including the $1s$ electrons and $1/1$ (s/p) basis set.⁴¹ The next shell of 22 Cu cations has been represented by total ion potentials (TIP's), generated from an one-electron Cu pseudopotential⁴¹ bearing a formal charge of +2. The calculation with the DDCI scheme^{35,36} have been performed with the programs written by Caballol *et al.*⁴² and Maynau *et al.*⁴³ The number of determinants included in the largest DDCI3 calculations with C_i point symmetry was 1 054 298.

For the concurrently performed density-functional (DFT) calculations we used the GAUSSIAN94 (Ref. 44) program package with a $6-3111+g$ all electron basis for Cu and $6-31g^*$ for all F anions. The TIP's and the set of point charges were the same used in the CI calculations. The functionals considered were the Becke's exchange functional³⁸ with Lee-Yang-Parr parametrization⁴⁵ of the Colle-Salvetti correlation functional.⁴⁶ These functionals have been employed within hybrid methods, B3LYP (Ref. 37) and BFLYP,^{24,25} where the true Hartree-Fock exchange term is mixed in different percentages with Becke's exchange functional. The DFT and CI calculations were all performed on an HP J282 workstation and on the previously mentioned SP2 machine of the Catalan Supercomputer Center (CESCA) in Barcelona.

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