

Ab initio study of magnetic interactions in KCuF_3 and K_2CuF_4 low-dimensional systems

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The *ab initio* cluster model approach has been used to study the electronic structure and magnetic coupling of KCuF_3 and K_2CuF_4 in their various ordered polytype crystal forms. Due to a cooperative Jahn-Teller distortion these systems exhibit strong anisotropies. In particular, the magnetic properties strongly differ from those of isomorphous compounds. Hence, KCuF_3 is a quasi-one-dimensional (1D) nearest neighbor Heisenberg antiferromagnet whereas K_2CuF_4 is the only ferromagnet among the K_2MF_4 series of compounds ($M = \text{Mn, Fe, Co, Ni, and Cu}$) behaving all as quasi-2D nearest neighbor Heisenberg systems. Different *ab initio* techniques are used to explore the magnetic coupling in these systems. All methods, including unrestricted Hartree-Fock, are able to explain the magnetic ordering. However, quantitative agreement with experiment is reached only when using a state-of-the-art configuration interaction approach. Finally, an analysis of the dependence of the magnetic coupling constant with respect to distortion parameters is presented. [S0163-1829(99)09831-8]

I. INTRODUCTION

The study of magnetic interactions in strongly correlated insulators has recently attracted interest due to three main motives. The most important one, no doubt, concerns high- T_c superconductivity because most of the cuprate superconductors exhibit strong antiferromagnetic interactions in the normal phase and this may play a role in fundamental theories of superconductivity.^{1,2} The second reason arises from the difficulty of conventional solid state band structure calculations to properly describe the electronic structure, magnetic interactions, and magnetic structures of these systems.² The third likewise important reason arises from the need to understand the strong anisotropies in crystal structures and magnetic ordering in low-dimensional systems and focus the interest of the present work. The low-dimensional term is used to describe crystal structures where some relevant properties can be fully explained without invoking the three-dimensional (3D) periodic structure of the solid. The magnetic order and most of the properties of the normal state of high- T_c cuprates can be described by invoking 2D CuO_2 planes only. This dimensionality is further reduced to 1D in ladder compounds^{3,4} where magnetic order within nearest neighbors in the Cu-O ladders does imply just one direction.

In the case of magnetic interactions and magnetic order, the appearance of low dimensionality has important consequences. For instance, the mean field approach to the Heisenberg Hamiltonian is not suitable and quantum fluctuations in the Heisenberg nearest neighbor model in one dimension have to be accounted for.⁵ Therefore, theoretical description of magnetic interactions in these low-dimensional systems faces the problems originated by the strong correlated nature of these wide gap ionic insulators. Hence, instantaneous electron-electron interactions must be explicitly accounted for in any *ab initio* theoretical approach aimed at properly describing these systems as insulators and at quantitatively predicting the extent of the magnetic coupling.² Similarly, quantum fluctuations have to be included to achieve a satisfactory agreement between theory and experiment when us-

ing the Heisenberg model Hamiltonian. In fact, quantum fluctuations and electronic correlation are two different ways to term the same effect, namely, the need to go beyond a mean field description of the exact or of the model Hamiltonian used in these theoretical approaches. In the case of *ab initio* approaches to magnetic coupling, inclusion of the subtle electronic correlation effects governing the magnitude of the magnetic coupling constant requires the use of sophisticated state-of-the-art methods. Much of the commonly used spin polarized band structure calculations based either on density functional theory (DFT) or in the Hartree-Fock approach fail to accurately describe the electronic and magnetic properties of this kind of insulators including those with 3D character.² On the other hand, a local or cluster approach enables the use of pure spin eigenfunctions and of highly correlated wave functions. As a result, calculated values of J are in agreement with experiment.⁶⁻¹⁶ This agreement is complete when specially designed configuration interaction expansions are variationally solved.^{13,14,17} The fact that the experimentally determined magnetic coupling constant and the *ab initio* cluster model calculated value quantitatively agree is the fingerprint of the local two-body character of the magnetic coupling constant.^{17,18}

In this work we extend the *ab initio* cluster model approach⁷⁻¹⁸ to the study of the electronic structure and magnetic coupling of KCuF_3 and K_2CuF_4 low-dimensional systems in their various ordered polytype crystal forms. Earlier neutron diffraction studies on KCuF_3 (Ref. 19) suggested that the KCuF_3 structure was slightly distorted from the cubic prototypical KNiF_3 one. This interpretation is in agreement with recent x-ray diffraction measurements²⁰ and with a particular orbital ordering of the magnetic orbitals claimed by Khomskii and Kugel^{21,22} based on the cooperative Jahn-Teller effect. This fact explained the actual distorted structure of KCuF_3 and also properly predicted that K_2CuF_4 will exhibit an analogous Jahn-Teller distorted structure with feeble ferromagnetic interactions in the magnetic planes.^{23,24} It is believed that the distortion from the ideal cubic or tetragonal structures, respectively, induces a strong anisotropy

in their mechanical and magnetic properties. Hence, KCuF_3 behaves as a quasi-1D nearest neighbor antiferromagnet Heisenberg system whereas K_2CuF_4 is the only ferromagnet representative of 2D Heisenberg systems in the K_2MF_4 ($M = \text{Mn, Fe, Co, Ni, and Cu}$) family.²⁵ Therefore, the interest in these systems arises from their electronic and crystal structures, related to the high- T_c superconductors and with different low-dimensional magnetic character. This is a challenge for a theoretical study and further motivation for a comparative analysis of its electronic structure and of its influence on the magnetic coupling constant.

II. EXTRACTION OF THE MAGNETIC COUPLING CONSTANTS

Previous cluster model studies using sophisticated configuration interaction techniques^{6–18} have shown that for wide gap ionic insulators, the magnetic coupling constant J is a local property that may be described correctly by means of a properly embedded finite model containing only two interacting magnetic centers. The Heisenberg Hamiltonian for such a cluster model reduces to

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

and, since for two interacting centers with $S = \frac{1}{2}$, as the Cu^{2+} cations in KCuF_3 and K_2CuF_4 , the triplet $|T\rangle$ and singlet $|S\rangle$ states are the only eigenstates of Eq. (1), it follows that

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

which allows us to obtain J from *ab initio* electronic structure calculations.

One may also apply unrestricted Hartree-Fock (UHF) and DFT based spin polarized solutions to the problem of magnetic coupling in ionic solids^{26,27} following a method similar to those earlier used by Noodleman and Davidson^{28,29} or by Bagus and Bennett.³⁰ In this approach the ferromagnetic, $|F\rangle$, state is rather well represented but one is forced to use a broken symmetry, $|BS\rangle$, solution for the antiferromagnetic, $|AF\rangle$, state. In a recent work³¹ it has been shown that for two $S = \frac{1}{2}$ localized magnetic moments J may be obtained as

$$J = 2(E_{|BS\rangle} - E_{|F\rangle}). \quad (3)$$

We must remark that the periodic, band theory, approach to magnetic systems is always based in the spin polarized approach and a broken symmetry (BS) solution is used to describe the antiferromagnetic phase.^{32–36}

III. SUMMARY OF CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES FOR KCuF_3 AND K_2CuF_4

Both KCuF_3 and K_2CuF_4 have perovskitelike structures isomorphous to the cubic KNiF_3 and the tetragonal K_2NiF_4 , respectively. In these structures, Cu^{2+} is a d^9 cation in an octahedral crystal field, hence e_g orbitals have different occupation and a Jahn-Teller (JT) distortion stabilizes the structure. The distortion on each copper center is equivalent and a few possible cooperative distortions of the solid structure exist depending on the cation coordination and the rest of the ions in the crystal. The appearance of elongated distorted octahedra has been theoretically explained by Khom-

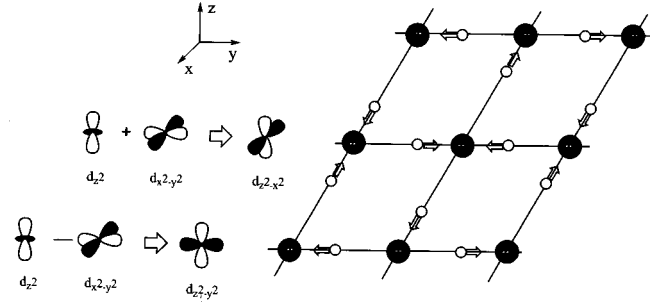


FIG. 1. Schematic representation of the ordering of the elongated axis of the distorted octahedra on *ab* planes. The magnetic orbital of each Cu^{2+} center, $d_{z^2-x^2}$ and $d_{z^2-y^2}$, are perpendicular to the elongated axis and are also shown.

sii and Kugel,^{21,22} from simple orbital arguments which consists in alternating $d_{z^2-x^2}$ - and $d_{z^2-y^2}$ -type orbitals arising from the two possible combinations of the $d_{x^2-y^2}$ and d_{z^2} pure atomic orbitals (cf. Fig. 1). For both KCuF_3 and K_2CuF_4 , this orbital alternation on neighbor copper centers in the *ab* planes results always in a feeble direct exchange interaction leading to a ferromagnetic interaction in the *ab* plane, $J_{ab} > 0$. In the case of KCuF_3 for each magnetic center in the *ab* plane there is always a magnetic center neighbor in the *c* direction which can interact by a strong superexchange mechanism, $J_c < 0$, and this system can be regarded as formed by linear antiferromagnetic chains in the *c* direction but with a feeble ferromagnetic interchain interaction. For K_2CuF_4 the additional nonmagnetic KF planes along the *c* direction block any magnetic interaction and the only magnetic interaction left is the weak ferromagnetic coupling between neighbor magnetic centers lying in the *ab* planes.

A. KCuF_3

In the KCuF_3 tetragonal perovskite, there are three Cu-F distances and two nonequivalent bridging F because the JT distortion on the Cu^{2+} centers slightly displaces the F ions from the midpoint of adjacent Cu sites in the *ab* planes (Fig. 1). Depending on the stacking of the *ab* planes along the *c* axis, KCuF_3 has two ordered polytype structures: twisted, *A* (Fig. 2), and untwisted, *D*.^{19,20} In a given sample these two polytype forms usually coexist and preparation of pure phases requires careful synthesis.

Susceptibility measurements and heat capacity curves³⁷ denoted a 1D antiferromagnetic behavior with a J value of -380 K. Neutron diffraction experiments¹⁹ found a magnetic order consisting in linear antiferromagnetic chains along the *c* axis with J_c again of ~ -380 K with a feeble interchain J_{ab} ferromagnetic coupling of $\sim +0.4$ K and with a Cu^{2+} magnetic moment of $0.5\mu_B$ confined in the *ab* planes. Values for J_c in the $[-406, -337]$ K range and $J_{ab} \sim +4$ K have also been reported.^{38–41}

Periodic UHF calculations³⁴ predict that KCuF_3 is a wide gap insulator with a KK ground state orbital ordering and that ordered, *A* and *D*, and disordered stacking polytype forms are almost isoenergetic. This study predicts that KCuF_3 has effectively 1D magnetic structure. The $J_c = -92$ K and $J_{ab} = +2$ K reported values are in qualitative

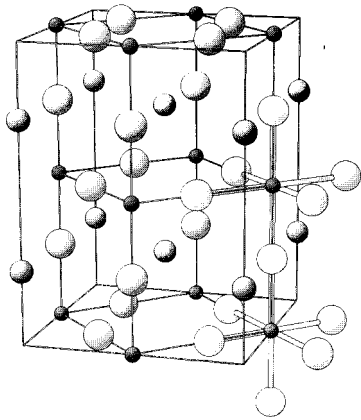


FIG. 2. The unit cell of the twisted, A, structure for KCuF_3 . Small (medium) dark spheres represent Cu^{2+} (K^+) cations and light large spheres represent F^- anions. The cluster model used to calculate J_c is also shown, thick lines link the atoms in the cluster model used in the calculations.

agreement with experiment but are too small because of the lack of electron correlation.^{32–35}

B. K_2CuF_4

K_2CuF_4 is a ferromagnetic ionic insulator with crystal structure derived from that of the ideal K_2NiF_4 crystal. In K_2CuF_4 the JT distortion displaces the F anions from the middle of the adjacent Cu centers, as in the KCuF_3 ab planes (Fig. 1). The K_2CuF_4 crystal structure has been unequivocally resolved and an ordered phase similar to that of ideal K_2NiF_4 was found.^{23,24} This is precisely the one chosen in the present study; the orthorhombic unit cell, containing four formula units, is represented in Fig. 3, with the basal plane of

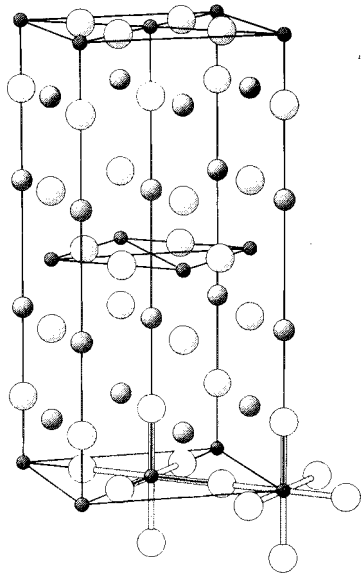


FIG. 3. The orthorhombic unit cell of K_2CuF_4 . Small (medium) dark spheres represent Cu^{2+} (K^+) cations and light large spheres represent F^- anions. The cluster model used to calculate J_{ab} is also shown, thick lines link the atoms in the cluster model used in the calculations. The basal plane of the K_2NiF_4 -type pseudocell is indicated in the middle of the figure.

the K_2NiF_4 -type pseudocell indicated in the center of the figure for comparative purposes.

K_2CuF_4 exhibits a $1.0\mu_B$ localized magnetic moment on each Cu atom (at $T=0$ K) lying on ab planes^{42–44} forming a quasi-2D Heisenberg ferromagnetic system at low temperature with a small XY anisotropy ($\sim 1\%$). The Curie temperature of this compound is 6.25 K,^{42–44} the magnetic coupling constant has been determined from thermal analysis,⁴⁴ and by neutron diffraction⁴³ and is in the range 15–23 K. The KK orbital ordering of the magnetic planes was also invoked to explain the observed magnetic order.⁴²

Recent theoretical works on electronic and magnetic properties of K_2CuF_4 are from local density approximation (LDA),⁴⁵ and from *ab initio* derived Hubbard Hamiltonian⁴⁶ studies. The LDA band structure calculations⁴⁵ were even unable to predict the distorted K_2CuF_4 structure and the undistorted structure was predicted to be metallic. Extended Hubbard Hamiltonian studies⁴⁶ were able to nicely reproduce the magnetic order of this compound. However, the accuracy of these model Hamiltonians strongly depends on the parameters used and predictions of physical magnitudes, so elusive as the magnetic coupling constants, from model Hamiltonians is of limited value.

IV. COMPUTATIONAL APPROACH

In this work we use a cluster model configuration interaction approach to obtain the relevant magnetic coupling constants for KCuF_3 and K_2CuF_4 . For KCuF_3 we consider J_c in A and D polytypes and J_{ab} in the D polytype. For K_2CuF_4 we consider J_{ab} in ordered K_2NiF_4 -type structures. For both compounds we have also investigated the effect of the JT distortion in the ab planes on J_c or J_{ab} , respectively, by using idealized, fictitious, structures, I , in which the structural parameters are those of the A polytype for KCuF_3 and those of the K_2NiF_4 -type structure for K_2CuF_4 but where distortion has been removed.

Local Cu_2F_{11} cluster model representations of the compounds have been used. These models contain two magnetic centers lying on the c axis or on the ab planes and are embedded in an appropriate crystal environment consisting of one shell of total ion potentials (TIPs),⁴⁷ and an array of point charges to adequately account for the Madelung potential (see Refs. 48 and 49). Further, nonempirical pseudopotentials are used to represent the He and Ne inner cores of outer F (Ref. 50) and Cu,⁵¹ respectively. For the bridging F^- anion all electrons are explicitly considered. The number of electrons corresponds to that of an ionic system although the complete final clusters are electrically neutral. The wave functions used in this work are flexible enough so as to include any possible covalent character albeit this has been shown to be very small.^{34,45} Pure spin wave functions of increasing complexity were obtained to describe the electronic structure of the central Cu_2F_{11} unit of the KCuF_3 and K_2CuF_4 cluster models. The wave functions are constructed from atomic orbitals expressed in a contracted Gaussian-type orbital (CGTO) basis set. For Cu we use a $(10s5p5d)$ primitive set contracted to $[4s3p3d]$ basis, for the bridge F anion the basis set is $(11s5p2d)$ contracted to $[4s3p2d]$, while for the remaining ligands we use a $[2s2p]$ contraction of the $(5s5p)$ primitive set. Improvements beyond the present ba-

sis set quality lead only to modest changes in calculated J values.^{7-10,12-18} A preliminary restricted open-shell Hartree-Fock calculation for the triplet state is carried out to generate a set of molecular spin orbitals.

First, we consider a complete active space configuration interaction (CASCI) wave function containing all Slater determinants that can be built by distributing the active electrons in the active orbitals. This CASCI is equivalent to the superexchange Anderson model.^{52,53} The CAS is defined by the two half filled orbitals arising from the JT splitting of the e_g manifold and contains two active electrons, therefore, giving rise to either triplet or singlet states. This model is limited because it neglects terms that involve excitations out of the CAS; these excitations contribute to the external correlation and correspond to important physical mechanisms necessary to correctly describe magnetic interactions.⁵⁴

Following previous works, the CASCI description is improved by making use of the difference dedicated configuration interaction (DDCI) method⁵⁵ (see also Ref. 17 for recent applications related to this work). Two different DDCI spaces have been considered. The first one, DDCI2, includes excitations, either holes and/or particles, with at most two inactive orbitals. When covalent effects are important the ML^+M^- configurations (where L is the bridging atom between the metal atoms) play an important role in enhancing the superexchange mechanism.¹⁷ These charge transfer configurations are included in the DDCI2 space as one-hole configurations, but their effective energy is too high unless instantaneous repolarization of these instantaneous physical situations is explicitly accounted for. This effect is included when considering the full DDCI list which includes configurations having up to two holes, one particle and one hole, two particles in the inactive orbitals and, hence, is often denoted as DDCI3. Both DDCI2 and DDCI methods have been used to compute the J values in various structures of KCuF_3 and K_2CuF_4 .

In order to provide an adequate comparison to available³⁴ and forthcoming solid state studies where configuration interaction techniques cannot be applied, we have computed the J values in KCuF_3 and K_2CuF_4 by using a spin polarized broken symmetry approach in Hartree-Fock, UHF, or DFT methods following the previous works by Martin and Illas.^{26,27} These BS calculations are carried out on the same cluster models but using all electron basis sets as in Refs. 26 and 27. The exchange-correlation functionals used include the well-known B3:LYP hybrid three-parameter functional which mixes the single determinant exchange (as in Hartree-Fock) with the gradient corrected Becke88 exchange functional, and uses the Lee-Yang-Parr gradient corrected correlation functional,⁵⁶ and a set of functionals which include an equal mixture of Fock and DFT [local or gradient-corrected, Becke88 (Ref. 57)] exchange and the correlation functional is either ignored or included in the LYP form,⁵⁸ for a detailed description see Ref. 27.

All CI calculations were carried out using the PSHF-CIPSI-CASDI chain of programs.⁵⁹ UHF and DFT calculations were performed using the GAUSSIAN94 program.⁶⁰

V. RESULTS

The theoretical values of magnetic coupling constants for KCuF_3 , J_c for A , D , and I structures and J_{ab} for the D -type

TABLE I. Magnetic coupling constants of KCuF_3 in A , D , and I structures (in K) obtained at different levels of theory using embedded Cu_2F_{11} cluster models.

Computational method	Structure A		Structure D		Structure I	
	J_c	J_c	J_{ab}	J_c	J_c	J_c
CASCI	-72.2	-73.6	+1.9	-109.6		
DDCI2	-187.5	-184.9	+1.2	-276.0		
DDCI	-344.0	-363.0	+6.5	-513.4		
Experiment ^{19,37-41}	[-405, -380]		~+4.0			
UHF	-83.8	-84.2	+4.4	-130.5		
B3:LYP	-680.9	-672.0	+46.4	-1137.9		
F-S:Null	-266.2	-261.9	+13.5	-402.1		
F-S:LYP	-290.9	-286.5	+12.0	-443.4		
F-B:LYP	-251.8	-247.8	+14.7	-398.8		

one are given in Table I whereas the J_{ab} for the I and experimental ordered structures of K_2CuF_4 are collected in Table II. An important general feature of all theoretical approaches, including the simplest UHF method, is the correct qualitative description of the magnetic ordering. All results show the effective quasi-1D magnetic structure of KCuF_3 ($J_c \gg J_{ab}$) and the 2D feeble ferromagnetic character of K_2CuF_4 . Another feature is the close similarity between the calculated J_c (at all levels of theory) for the A and D structures of KCuF_3 , in agreement with experiment.

The CI calculations show a systematic improvement of the theoretical results which parallels the degree of complexity of the particular CI expansion used. The CASCI calculations provide a qualitative description only. The DDCI2 results lead to a semiquantitative agreement with the experimental values recovering roughly 50–70% of the experimental J value. This level of theory permits a fair description of magnetic coupling using rather small CI spaces; for the clusters used in this work the dimension of the DDCI2 space is of $\sim 10^4$ – 10^5 determinants. A further improvement is achieved when considering the full DDCI list ($\sim 3 \times 10^5$ – 2×10^6 determinants). The results are now in very good agreement with experimental results for KCuF_3 and K_2CuF_4 , in accordance with results for the more symmetric KNiF_3 , K_2NiF_4 , and La_2CuO_4 systems.¹⁷ This is be-

TABLE II. Magnetic coupling constants of K_2CuF_4 in experimental and I structures (in K) obtained at different levels of theory using embedded Cu_2F_{11} cluster models.

Computational method	Experimental structure	Structure I
	J_{ab}	J_{ab}
CASCI	+3.4	-7.6
DDCI2	+5.1	-21.3
DDCI	+14.6	
Experiment ⁴²⁻⁴⁴	[+15, +23]	
UHF	+6.5	-5.7
B3:LYP	+86.7	-53.2
F-S:Null	+23.1	-21.9
F-S:LYP	+25.1	-23.9
F-B:LYP	+21.2	-21.1

cause the DDCI space includes almost all important physical mechanisms determining the magnitude of the J in this kind of ionic solids. The improvement of the numerical results achieved when the DDCI2 space is enlarged to form the full DDCI space is due to the inclusion of the single excitations of the Cu-F charge transfer determinants which account for the orbital relaxation of these instantaneous ionic forms. Hence, DDCI is able to mimic the orbital relaxation effects accounted for in the nonorthogonal configuration interaction (NOCI) approach used by Van Oosten, Broer, and Nieuwpoort¹⁴ in their study of superconductor parent compounds. The use of the full DDCI list includes the same effects and can be applied to cases such as KNiF_3 where NOCI becomes prohibitive. We must point out that the use of the full DDCI list is not necessary. In fact, it will be enough to extend the DDCI2 space by including the rather small list of the single excitations of the Cu-F charge transfer determinants. The use of the full DDCI space is just convenient for technical reasons.

Now, we turn our attention to the BS approaches which can also be employed in solid state periodic calculations. The crude UHF method has been included to properly compare the numerical results from a local cluster model approach to those that correspond to a fully periodic description as reported in previous works.¹⁰ For KCuF_3 the cluster results nicely reproduce those arising from the periodic calculations by Towler, Dovesi, and Saunders.³⁴ Hence, for either J_c or J_{ab} we found -86 and $+4$ K which have to be compared with -92 and $+2$ K reported in Ref. 34. This fact is another clear fingerprint of the local, two-body, character of the magnetic coupling constant in the Heisenberg Hamiltonian.^{10,17,18} For K_2CuF_4 the BS UHF also correctly describes the magnetic ordering. However, one must be aware of the fact that these UHF, cluster or periodic, calculations lead to values of J that are too small compared to experiment because of the lack of external correlation. The UHF provides a crude approximation to the CASCI and, hence, cannot go beyond the Anderson model. One must recognize that the magnitudes of the ferromagnetic coupling constants of K_2CuF_4 and J_{ab} of KCuF_3 are very small and results from this BS UHF method are surprisingly close to the experimental value. The DFT results have been included because they currently provide the only way to study magnetic coupling fully exploiting the 3D character of these systems. We must remark that all methods correctly predict the KK orbital ordering. The fact that all methods predict this KK orbital ordering is a consequence of the electronic structure which is the driving force for the crystal structure. Therefore, the magnetic order is a consequence of the electronic structure and not vice versa.

With respect to the numerical values predicted by the different DFT approaches we find the same trend as in the works by Martin and Illas.^{26,27} The effect of the correlation functional is minor and all the action is taken by the exchange part. As in previous works,^{26,27} a reasonable numerical description is only found when Hartree-Fock and DFT, local or gradient-corrected, exchange are mixed on an equal footing. We must stress that the semiempirical B3:LYP functional which is very popular in chemical applications and performs very well in thermochemistry^{61,62} gives values for J that are systematically 80% or more in excess with respect to the experimental ones for ferromagnetic or antiferromagnetic

couplings. The rest of the hybrid functionals obtain numerical values close to the DDCI2 ones for all the structures. In order to bring the B3:LYP close to the experimental values one must assume that, in spite of having an expectation value of ~ 1.000 for the total square spin operator, the energy of the BS B3:LYP solution is that of the pure singlet state.^{63,64} This assumption will also violate the mapping procedures discussed above and will lead to the absurd consequence that two equivalent BS approaches such as UHF or DFT have to use two different mappings (see Ref. 10) to compute the magnetic coupling constant and to the absurd conclusion that the antiferromagnetic state of a periodic system leads to the energy of the pure singlet state.

To provide further arguments about the influence of the electronic structure on the magnetic order let us have a rapid insight into the ideal, I , structures, in which the distortion parameters in the ab planes have been set equal to zero. The consequence is that the magnetic orbitals become almost pure d_{z^2} atomic orbitals and the KK ordering disappears. For KCuF_3 this effect enhances the superexchange mechanism along the c axis because the overlap between the magnetic orbitals and the F bridge p_z orbitals increases. Therefore, J_c becomes more negative and the effective 1D character of the magnetic structure is maintained. For K_2CuF_4 the removal of the structural distortion causes a different effect on J_{ab} . In terms of the simple Anderson model where one considers that the magnetic coupling constant has simply a weak direct exchange contribution plus a stronger antiferromagnetic superexchange contribution to J , the removal of the distortion maximizes the overlap between the magnetic orbitals and the F bridge $p_{(x,y)}$ orbitals. Hence, the superexchange mechanism contribution dominates over the direct exchange contribution and the sign of the magnetic coupling constant is reversed while maintaining the 2D magnetic structure. A similar line of reasoning holds for J_{ab} in KCuF_3 .

VI. CONCLUSIONS

In this work difference dedicated configuration interaction methods have been applied to properly embedded cluster models of the A - and D -type structures of KCuF_3 , ordered K_2CuF_4 structure and the respective ideal, I , undistorted, structures to investigate the physical contributions to the magnetic coupling constants and to provide accurate theoretical values of this elusive physical property. To provide adequate comparison to forthcoming periodic calculations, several polarized UHF and DFT formalisms using a broken symmetry approach have also been used. In spite of using cluster models which explicitly consider two magnetic centers only, the DDCI approach reaches a quantitative description of the magnetic coupling constant for all the experimental structures. The success of the DDCI method lies in the inclusion of the instantaneous relaxation of the Cu-F charge transfer forms. This effect is crucial to correctly describe the magnetic coupling constant in this class of wide gap ionic insulators. The DFT results provide a qualitative agreement with experiment for KCuF_3 and even quantitative agreement for K_2CuF_4 . However, the widely used B3:LYP functional gives J values exceeding the experimental ones by a factor of 1.5 to 4 for ferromagnetic or antiferromagnetic interactions. The rest of the hybrid functionals explored in this work re-

cover roughly 60% of the experimental value for antiferromagnetic interactions and match the experimental one for ferromagnetic interactions. The orbital ordering described by Khomskii and Kugel⁷ is predicted at all levels of theory used in this work provided the experimental structures of both solids is used as external input. We must stress the fact that crystal structure results from the electronic structure, and magnetic order is a consequence of this electronic structure. This assertion is supported by computational experiments where the distortions in the *ab* planes are eliminated, resulting in ideal *I*-type structures. Calculations on these *I* structures reveal that the directionality of the magnetic orbitals on each Cu²⁺ center is enhanced and has two different effects in the two compounds. In KCuF₃ this larger directionality increases the magnitude of the magnetic coupling constant along the *c* axis because superexchange mechanism is favored due to an increasing in overlap between open shells of

neighbor magnetic centers and the bridging ligand. In K₂CuF₄ the overlap between magnetic orbitals of neighbor Cu²⁺ centers and F⁻ orbitals is maximized and the weak enhancement of the antiferromagnetic contribution to *J* is slightly augmented reversing the sign of *J* for the interaction in the *ab* planes.

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