Ab initio study of the magnetic interactions in the spin-ladder compound $SrCu_2O_3$

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A wide range of experimental, semiempirical, and theoretical values have been reported in the literature for the magnetic coupling parameters of the two-leg ladder compound $SrCu_2O_3$. We apply quantum chemical and density functional techniques to calculate accurate *N*-electron wave functions or densities for two different Cu_2O_7 clusters that represent the leg ($J_\parallel$) and rung ($J_\perp$) of the ladder. Our data indicate that $J_\parallel$ is slightly larger than $J_\perp$ ($J_\perp/J_\parallel \approx 0.9$) with $J_\perp = -139$ meV (-1670 K) and $J_\parallel = -156$ meV (-1870 K). Recent experimental data indicate a more strongly anisotropic ratio, $J_\perp/J_\parallel \approx 0.5$. The origin of the difference is unclear, as our *ab initio* estimates of $J_\perp$ and $J_\parallel$ seem to be converged with respect to the size of the basis set, the level of electron correlation, and the size of the cluster. However, we also find a surprisingly strong ferromagnetic interladder interaction which may play a role in resolving this discrepancy. [S0163-1829(99)01126-1]

I. INTRODUCTION

Over the last ten years, condensed-matter chemists and physicists have been exploring the surprising richness of cupric oxides or cuprates. A wide variety of compounds have been synthesized and investigated. One of the most important classes of cupric oxides is formed by the high-T_c superconductors and their undoped parent compounds. These compounds are characterized by (virtually) isolated CuO_2 planes formed by corner-sharing CuO_4 squares in which all copper ions are connected to four other copper ions by a linear Cu-O-Cu bond. These bonds give rise to strong antiferromagnetic interactions and, hence, these compounds can be classified as two-dimensional antiferromagnets. Moreover, the magnetic spin moments of the undoped materials show long-range order at low temperatures. Another interesting class of cuprates is formed by the so-called antiferromagnetic copper oxide chains such as Sr_2CuO_3, which have the characteristic feature of corner-sharing CuO_4 squares in one direction only. In contrast to the two-dimensional antiferromagnet, the ground state of the one-dimensional spin-1/2 system can be solved exactly within the Heisenberg model Hamiltonian.[1] It is well-known that this exact ground state does not show true long-range antiferromagnetic order.

The discovery in the early 1990s of the $Sr_{n-1}Cu_nO_{2n-1}$ (with $n \geqslant 2$) series by Hiroi *et al.*[2] opened a different direction in the field. The compounds in this series are built from *n* one-dimensional chains in which the copper ions in adjacent chains are coupled by oxygen centers to form so-called *n*-leg spin ladders. The magnetic interaction between the ladders is rather small since ladders are connected to each other by a Cu-O-Cu bond of $\sim 90°$ (see Fig. 1). In principle, the spin ladders interpolate between the one-dimensional and the two-dimensional case: two interacting chains for $n=2$, while for very large *n* values a two-dimensional CuO_2 plane appears. However, intensive theoretical and experimental investigations showed that the progression from one to two dimensions is far from smooth. Even-leg ladders show a spin gap,[3–11] neither observed in the copper oxide chains nor in two-dimensional antiferromagnets. On the other hand, the odd-leg ladders do not possess a spin gap and behave as effective one-dimensional chains.[6,9–13] The appearance of a spin-gap in the even-leg ladders gives rise to a finite spin-spin correlation length as $T \rightarrow 0$, whereas the spin-spin correlation function of the odd-leg ladder is similar to the one of the single chain.[6,14–16] The spin ladders also attracted much attention because of the possible appearance of superconductivity upon doping the ladders with holes.[4,5,17,18] Uehara

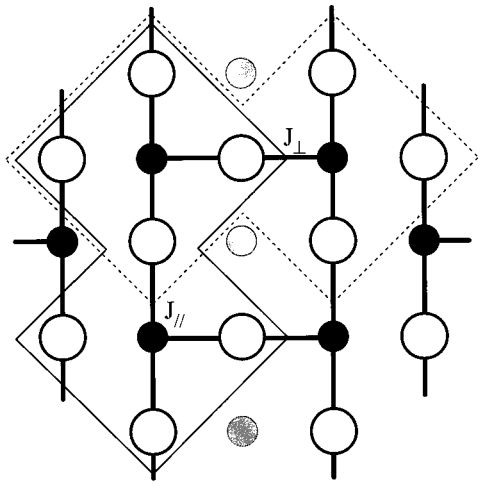

FIG. 1. Schematic view of the structure of the two-leg ladder $SrCu_2O_3$. Black circles represent Cu; open circles O; and gray circles Sr, which are situated above and below the Cu_2O_3 plane. The centers inside the area enclosed by the thin solid line form the Cu_2O_7 cluster for the leg and those inside the area enclosed by the thin dotted line the cluster for the rung. The thick lines represent the strongly antiferromagnetic Cu—O—Cu bonds, from which emerges the ladder structure. The coupling parameter $J_\parallel$ is that along the legs, and $J_\perp$ that along a rung.

et al. have actually been able to demonstrate superconductivity in a spin-ladder compound recently.[19,20] Comprehensive reviews of all interesting phenomena of the spin ladders, not only those of the $Sr_{n-1}Cu_nO_{2n-1}$ series but also of other spin-ladder compounds such as $LaCuO_{2.5}$ and $Sr_{14}Cu_{24}O_{41}$, are given by Dagotto and Rice,[10] Rice,[11] and Maekawa.[18]

An important parameter in theoretical models of the electronic structure of cupric oxides, either two-dimensional antiferromagnets, spin chains, or ladder systems, is the effective magnetic coupling constant J, which parameterizes the strength of the magnetic interaction between the spin moments on the Cu^{2+} ions. The magnitude of J is well established for the two-dimensional antiferromagnets, e.g., the magnetic interactions in the parent compound La_2CuO_4 are generally considered to be characterized accurately by a J of -130 meV. However, for the lower-dimensional magnetic systems the situation is less clear. The best experimental realizations of one-dimensional spin-1/2 chains are the compounds Sr_2CuO_3 and Ca_2CuO_3. For these compounds J values for the intrachain coupling have been reported ranging from -140 meV to -260 meV.[21]

An extra complication arises in the spin-ladder systems. In principle, there are now two different J's, one for the interaction along the legs and one along the rungs of the ladder. Although both the legs and the rungs are built from similar linear Cu—O—Cu bonds, the possibility cannot be dismissed that $J_\parallel$ (along the legs) differs from $J_\perp$ (along the rungs). Given the similarity in Cu—O bond distances along legs and rungs, one would certainly expect a nearly isotropic situation ($J_\perp/J_\parallel=1$). However, for the simple two-leg ladder $SrCu_2O_3$, values of $J_\parallel$ have been reported ranging from -70 to -158 meV and ratios ranging from isotropic ($J_\perp/J_\parallel=1$) to strongly anisotropic coupling ($J_\perp/J_\parallel=0.5$).[7,9,22–27] If the magnetic interactions in the spin-ladder compounds are indeed best described by a parameter set with $J_\parallel \gg J_\perp$, the intuitive picture of the ground-state wave function as rung singlets with weak antiferromagnetic interaction along the legs[11] may need to be reconsidered.

The first experimental estimates of J were derived from measurements of the spin gap Δ.[7,9] Earlier theoretical studies had established the relation between the spin gap and the magnetic coupling parameters. For isotropic coupling, it was demonstrated that $\Delta \approx -0.5J$.[3,4,6,15] The nuclear-spin-lattice relaxation rate measurements of Ishida *et al.*[7] and Azuma *et al.*[9] lead to a value of the spin gap of 680 K (56 meV). Assuming isotropic coupling, the authors arrived at an estimate of J of -113 meV. In addition, Azuma *et al.* also performed measurements of the magnetic susceptibility as a function of the temperature. This results in a Δ of 420 K (35 meV) and, hence, a J of -70 meV. Azzouz *et al.*[24] were able to fit the data of Azuma *et al.* with a unique set of parameters. The assumption of isotropic coupling was given up and the following J's were reported: $J_\parallel=-71$ meV and $J_\perp=-51$ meV, which corresponds to a ratio $J_\perp/J_\parallel=0.72$. Sandvik *et al.*[23] calculated the magnetic susceptibility, spin-echo decay rate, and spin-lattice relaxation rate in good agreement with experimental data and extracted from these functions values for $J_\parallel$ and $J_\perp$. The best agreement was obtained for a ratio of 0.8 with $J_\parallel=-91$ meV and $J_\perp=-73$ meV. It must be noted that these parameters give rise to an anomalous g factor of ≈ 1.5. In the fit of the magnetic susceptibility presented by Johnston,[22] no such anomalous g factor appears, however, his results show rather strong anisotropy (a ratio of 0.5) and also a somewhat large value for $J_\parallel$ (158 meV) compared to previous estimates. Nevertheless, this interpretation of the magnetic interactions in $SrCu_2O_3$ has recently been confirmed by two different groups. Eccleston *et al.*[26] report neutron-scattering experiments on the spin-ladder compound $Sr_{14}Cu_{24}O_{41}$ which is composed of layers of spin ladders equivalent to the ones found in $SrCu_2O_3$ intermediated by layers composed of CuO_2 chains. These measurements give a ratio of the two J values of 0.55 and absolute values are estimated as -130 and -72 meV for $J_\parallel$ and $J_\perp$, respectively. Imai *et al.*[27] have published ^{63}Cu and ^{17}O NMR studies of the same compound and they reach the conclusion that $J_\perp/J_\parallel=0.5$, with $J_\perp=-79\pm25$ meV. Table I collects the experimental, semiempirical, and theoretical values of $J_\parallel$ and $J_\perp$ mentioned in this paragraph.

TABLE I. Overview of parameters reported in the literature for the strength of the magnetic coupling in $SrCu_2O_3$.

$J_\perp/J_\parallel$	$J_\parallel$ (meV)	$J_\perp$ (meV)	Refs.
1	-113	-113	7,9
1	-70	-70	9
0.5	-158	-79	22
0.8	-91	-73	23
0.72	-71	-51	24
1	-133	-133	25
0.55	-130	-72	26
0.5	-158 ± 50	-79 ± 25	27

So there now appears to be a consensus forming for a strong anisotropic ratio. A possible origin for this effect might be the different Cu-Cu distances in $SrCu_2O_3$ (3.934 Å for the leg and 3.858 Å for the rung). Note, however, that the shorter distance, and hence presumably larger magnetic interaction, is along the rung. This contradicts the experimental determination $J_\perp/J_\parallel \approx 0.5$. Another possibility might be differences in the Madelung potential for the oxygen centers mediating the superexchange interaction. In $SrCu_2O_3$, there is a difference of nearly 1 eV, the Madelung potential is 22.44 eV for the leg and 21.35 eV for the rung, assuming formal charges of $+2$, $+2$, and -2 for Sr, Cu, and O, respectively. Figure 1 illustrates the fact that the oxygen on the leg has five near neighbors (three Cu^{2+} and two Sr^{2+} ions), while that on the rung has six (two Cu^{2+} and four Sr^{2+}). This local coordination difference can affect not only the Madelung potential at the oxygen site, but also the polarization of the Cu—O—Cu linkages. However, the magnitudes of the oxygen Madelung potentials implies that the O-2p $\rightarrow$Cu-3d charge transfer energy is smaller along the rung. This suggests a larger J along the rung and $J_\perp/J_\parallel>1$, again in contradiction with experiment.

There are thus two unexpected results here. The first is the large anisotropy, and the second is that the ratio is opposite to what we would expect in terms of bond lengths and Madelung potentials. In this paper we present the results of an *ab initio* quantum chemical study of the magnetic coupling parameters in $SrCu_2O_3$. These parameters are obtained by mapping spin eigenfunctions of the exact (nonrelativistic) Hamiltonian of a given material model onto the Heisenberg

Hamiltonian. This approach does not involve the fitting of any data to any kind of analytical function and only depends on the quality of the approximated eigenfunction obtained from the calculation and the appropriateness of the material model applied.

Typically, the materials of interest are represented by a cluster of 5–20 all-electron atoms embedded in an electrostatic background that accounts for the rest of the crystal. Although this seems a rather poor description for a periodic structure, several reasons can be given to justify the embedded cluster approach to investigate the magnetic interactions in ionic solids. First, we mention that empirical estimates of the magnetic coupling constants are usually extracted from experimental data with the help of the Heisenberg Hamiltonian. This operator normally contains two-body operators only, which implies that a cluster with two magnetic centers is sufficient. Furthermore, it has been demonstrated for several ionic compounds (e.g., $KNiF_3$, K_2NiF_4, NiO, La_2CuO_4) that the magnetic coupling parameter J does not hide any possible interactions between more than two magnetic moments.[28] In addition, it has been found that the magnetic interactions are completely additive in these compounds,[28–30] and hence, magnetic coupling parameters can be deduced from an appropriately chosen cluster model embedded in an accurate background. The question remains of the quality of the calculated wave function. It is well-known that it is essential to account for the very large electron correlation effects in the cuprates in order to obtain meaningful estimates of the magnetic coupling parameter. Modern quantum chemical techniques combined with extensive computational resources permit accurate approximations to the exact eigenfunction or to the differences in energy eigenvalues of the exact eigenfunctions. Starting from a mean-field approximation, i.e., the Hartree-Fock wave function, different computational schemes can be applied to calculate wave functions that have included the major part of the electron correlation effects. In combination with the above-mentioned considerations about the material model, theoretical estimates of magnetic coupling parameters have been obtained in close agreement with experiment for a wide variety of ionic solids.[31–38]

In the remaining part of this paper, we present the application of *ab initio* quantum chemical techniques to the problem of the magnitude of the magnetic coupling parameters in the ladder compound $SrCu_2O_3$. In the next section, we give a short explanation of how one obtains estimates of the magnetic coupling parameters from *ab initio* cluster calculations, and moreover, a description of the computational methods and material model used. After that, we carefully analyze our results, in which attention is focused on the validity of the applied material model and the quality of the approximated eigenfunctions of the cluster Hamiltonian. The last section contains a summary and a further discussion of the results.

II. MATERIAL MODEL

The spin-ladder $SrCu_2O_3$ is modeled by two different clusters, as illustrated in Fig. 1. One Cu_2O_7 cluster, which has D_{2h} local symmetry, is used to extract a J value for the rung and another Cu_2O_7 cluster, which has C_{2v} local symmetry, models the interaction along the leg. Some test calculations are performed for a Cu_4O_{10} cluster from which J values for leg and rung can be extracted at the same time, and finally, we use a Cu_2O_6 cluster to calculate the interladder magnetic interaction. All these clusters are embedded in an electrostatic background represented by optimized point charges that reproduce the Madelung potential in the whole cluster region with an accuracy better than 1 meV. To avoid an artificial polarization of the electrons of the cluster towards the point charges, we also include the short-range electrostatic repulsion between the cluster atoms and their near neighbors in the Cu_2O_7 clusters. Because of the quantum-mechanical nature of this short-range interaction, the most desirable approach would be to extend the size of the cluster treated *ab initio*. Unfortunately, this is computationally too demanding and therefore, we apply a more approximate representation of the interaction by representing the ions in the direct environment of the cluster with total ion potentials (TIP's).[39] We use the crystal structure as determined experimentally by Hiroi *et al.*[2]

The Cu^{2+} cations in the $SrCu_2O_3$ crystal are characterized electronically by their local electronic ground state ^2D, arising from the d^9 open-shell configuration. Two interacting copper cations can be coupled to form either a singlet or a triplet function. Under the assumption of a common orbital part for these two functions, the eigenvalues of the Heisenberg Hamiltonian ($-1/4J$ for the triplet and $3/4J$ for the singlet function) are directly related to the energy expectation values of the full electronic Hamiltonian. This allows us to extract estimates of the magnetic coupling parameters from our spin-restricted calculations by the relation $E_s - E_t = J$. From this relation it is clear that a negative J arises when the antiferromagnetic ordering is the preferred one. For the cluster model with four copper cations, the values of J are derived in a similar, although slightly more complicated way.[40] On the other hand, for the spin-unrestricted approaches [unrestricted Hartree-Fock, density-functional theory (UHF, DFT)] no such relationship exists. Noodleman and Davidson[41] have derived the relationship between the eigenvalues of the spin-unrestricted cluster wave functions and the true singlet-triplet energy eigenvalues. Under the assumption of zero overlap between the open-shell orbitals of the broken symmetry solution representing the antiferromagnetic (AF) state, this relation reads: $E_{AF} - E_F = 1/2J$, as proposed by Caballol *et al.*[42] Again a negative J indicates that antiferromagnetic ordering is the most stable one. We refer to previous work[38,43] for a more comprehensive description of how to obtain J values from *ab initio* calculations.

III. COMPUTATIONAL METHODS

The original ideas of superexchange formulated by Anderson and Nesbet[44,45] can be followed by performing a CASCI (complete active space CI) in which the active orbitals are the open-shell orbitals on the Cu^{2+} ions. This choice of the N-particle basis normally reproduces the correct sign of J, although the value computed is usually only 20–30 % of the experimental. Several approaches exist—and have been applied successfully over the last few years—to improve the CASCI approximation. We use methods based on the understanding that the large majority of the determinants outside the CAS space contribute equally to the energy ex-

TABLE II. Dependency of the magnetic coupling parameters on the basis set and the material model. Basis **A** consists of the 6-3111+G basis for Cu, and the 6-31G* basis for O. Basis **B** is as **A** augmented with an extra f-type function on Cu. In basis **C** the TIP's for Sr are replaced by the LAN2MB basis set.

	$J_\perp/J_\parallel$		$J_\parallel$ (meV)		$J_\perp$ (meV)	
	UHF	B-F: LYP	UHF	B-F: LYP	UHF	B-F: LYP
Basis **A**	0.94	0.92	−39.2	−122.4	−36.8	−112.4
Basis **B**	0.94	0.92	−38.8	−121.0	−36.4	−111.0
Basis **C**	0.91	0.87	−36.5	−108.9	−33.2	−95.2

pectation value of the singlet and the triplet wave functions.[46,47] By skipping these determinants, a relatively short list of determinants can be constructed that directly contribute to the energy difference of the two spin states. Under the assumption of a reference space with equal expectation values for triplet and singlet, the list of contributing determinants only contains singly and doubly excited determinants with the restriction of at most two holes in the inactive orbitals, one hole in the inactive plus one particle in the secondary, or two particles in the secondary orbitals. The effect of the determinants in this list can be evaluated either with second-order perturbation theory—here referred to as MP2-2—or by a complete diagonalization of the interaction matrix, i.e., by configuration interaction, here referred to as DDCI2.[47,48] This approximation already gives rather good results, but it has been found recently[49–51] that adding some well-defined determinants to the CI space yields a significant improvement of the results. The extra determinants treated in this approach, labeled as DDCI3,[47,48] are characterized by at most one hole in the inactive orbitals plus two particles in the secondary, or two holes in the inactive and one particle in the secondary orbitals. These determinants are precisely the ones that cause a relaxation of the configurations connected with a charge transfer excitation from the bridging ligand to a copper cation, a contribution which has been found extremely important by van Oosten *et al.*[32,33] For a discussion of the way in which these correlations modify the charge-transfer energy, see Ref. 31.

The other computational schemes applied are less well grounded but are important in the context of solid-state physics. These methods are all so-called unrestricted, or spin-polarized formalisms, i.e., the wave functions (or densities) are no longer necessarily eigenfunctions of $\hat{S}^2$. Within the UHF (unrestricted Hartree-Fock) calculations, the unrestricted equivalent of CASCI, wave functions are constructed for the ferromagnetic and antiferromagnetic states in the cluster model. The wave function for the ferromagnetic state approaches the maximum m_s component of the spin-restricted triplet wave function. However, the wave function of the AF state corresponds to a broken symmetry solution, a mixture of the true $m_s=0$ singlet and triplet wave functions.[41,42,52] Again, the estimate of J computed with this method has the right sign, but usually only a small fraction of the experimental value is obtained. Density-functional theory (DFT) seems to be a very promising method to tackle this shortcoming. The method offers a possibility to improve the J value computed in the Anderson model at a lower computational cost than the traditional restricted quantum chemical methods. The simplest and most widely used approximation for the unknown part of the density functional, usually referred to as the exchange-correlation potential, is the local-density approximation (LDA), in which the functional is derived for a noninteracting electron gas. However, it is well known that LDA is not able to reproduce the insulating character of many transition-metal compounds, moreover it has been shown lately that the magnetic interaction parameter is poorly estimated by this method.[38] Improvement on the correlation potential does not have a large effect. A gradient corrected exchange potential does improve the situation, although the computed values are still not comparable to experimental values. Illas and Martin[37,38] showed that with hybrid methods accurate estimates of J can be calculated. We apply the so-called B-F:LYP approximation for the exchange-correlation functional.[37,38,53–55] This functional combines in equal parts the exact Fock exchange functional with Becke's 1988 gradient corrected exchange functional. The Lee-Yang-Parr gradient-corrected functional[56] is used for the correlation part. In addition, we examine the popular B3:LYP hybrid functional.[57,58]

The calculations reported in this article have been performed with the PSHF-CIPSI-CASDI chain of programs,[59] with GAUSSIAN 94 (Ref. 60) and with MOLCAS 4.0.[61]

IV. RESULTS

Within the material models for rung and leg as described above, N-electron wave functions for the singlet and triplet states or for the ferromagnetic and antiferromagnetic states are expanded in an identical set of one-particle functions. Table II presents a set of calculations in which the one-particle space is systematically improved. We have only investigated the UHF and B-F:LYP approximations in this way because the spin-restricted methods, especially DDCI3, are computationally much more demanding. Basis set A in the Table uses the 6-3111+G basis[62–64] for Cu $(19s,13p,7d)/[7s,6p,5d]$ and the 6-31G* basis $(10s,4p,1d)/[3s,2p,1d]$ for all oxygen atoms in the cluster.[65] Table II shows that both spin-unrestricted methods do reproduce the experimental observation that $J_\perp/J_\parallel<1$, although the ratio is only about 0.9 (It should be noted that preliminary calculations utilizing effective core potentials for both Cu and O atoms give an inverted ratio, that is $J_\perp/J_\parallel>1$). The difference in the absolute magnitudes of the coupling parameters in the UHF and hybrid DFT (B-F:LYP) is expected. The UHF approximation is well-known to underestimate J because it places the O-$2p\rightarrow$Cu-$3d$ charge-transfer energy too high. In previous research, we found that the B-F:LYP approximation yields ~95% of the experimen-

TABLE III. *Ab initio* estimates of the magnetic coupling parameters for leg and rung in $SrCu_2O_3$. The following contracted basis sets are applied: Cu $(5s,4p,3d)$, bridging O $(4s,3p,1d)$, and the edge oxygens $(3s,2p)$.

Method	$J_\perp/J_\parallel$	$J_\parallel$ (meV)	$J_\perp$ (meV)	J_{inter} (meV)
CASCI	0.91	−23.9	−21.7	1.0
MP2-2	0.92	−62.2	−57.4	
DDCI2	0.91	−83.8	−76.1	
DDCI3	0.89	−155.8	−139.3	12.5

tal coupling constant. The B3:LYP functional yields values that are clearly outside the experimental range, more than a factor of 2 larger than the corresponding B-F:LYP calculation. This has been observed before for other compounds as well,[38] and therefore, we do not consider this functional in any further calculations.

Next we introduce an *f*-type Gaussian function centered on Cu in the one-electron basis set (basis *B*) to permit polarization of the charge distribution of the Cu ions. This augmentation of the basis set does not give rise to significant changes in the calculated magnetic interaction parameters. The ratio remains constant, while the absolute values are lowered by not more than 0.6 meV. A larger change in the calculated values can be observed when the TIP description of the Sr^{2+} ions around the Cu_2O_7 clusters is replaced by an explicit description with basis functions of the valence electrons, albeit by a minimal, LAN2MB basis set[66] (basis *C*). Both $J_\perp$ and $J_\parallel$ decreases by approximately 10% and the ratio of both parameters is slightly smaller now. These changes are mainly explained by a size effect: The TIP used to represent Sr^{2+} was derived for neutral Sr and because neutral Sr is significantly larger than Sr^{2+}, the short-range repulsion between cluster and environment, which is primarily due to Pauli repulsion, is overestimated by the TIP. With the explicit representation of the Sr^{2+} valence electrons, we introduce extra ions into the cluster model with a smaller radial extent and hence, a more realistic description of the short-range repulsion.

As stated in the Introduction, it has been shown in several studies that for a variety of ionic solids the magnetic interactions are genuinely local and entangle two-body interactions only. For $SrCu_2O_3$ we can test this finding by defining the cluster such that it includes both legs and rungs. For this purpose, a Cu_4O_{10} cluster is constructed that contains two subsequent rungs along the legs of the ladder. The unpaired electrons on the four copper ions give rise to one quintet spin function, three different triplet spin functions and two singlet spin functions. The energy eigenvalues are determined in a CASCI, i.e., the Anderson model, and we apply the following all-electron one-particle basis:[67–69] Cu $(21s,15p,10d)/[5s,4p,3d]$; bridging O $(14s,9p,4d)/[4s,3p,1d]$; and all other O $(10s,6p)/[3s,2p]$. From the energy differences of all the spin eigenfunctions $J_\parallel$ and $J_\perp$ are calculated as −21.7 and −23.9 meV, respectively. The ratio $J_\perp/J_\parallel$ is 0.92. The *J* values obtained in the CASCI calculation from separate clusters for rung and leg, given in Table III, deviate less than 1% from the values obtained for the large cluster, in agreement with the earlier findings for other compounds that *J* does not have included collective interactions.

We now report the results of spin-restricted calculations in which all the above-mentioned considerations are taken into account in order to obtain reliable *ab initio* estimates for $J_\perp$ and $J_\parallel$. The one-particle space is equal to the one used for the Cu_4O_{10} cluster (*vide infra*), the short-range repulsion is included in the description of the electronic structure by replacing the infinitely small point charges nearest to the bridging oxygen by frozen charge distributions. These charge distributions are obtained in Hartree-Fock calculations on a $[Sr_4]^{8+}$ (for the rung) or a $[Sr_2Cu]^{6+}$ (for the leg) fragment embedded in the point charges used in all calculations and the ions of the Cu_2O_7 cluster are replaced by their formal ionic charges. Subsequently, these charge distributions are combined with their respective cluster charge distribution by a Gramm-Schmidt orthogonalization. In the calculations of the spin states the $[Sr_4]^{8+}$ and $[Sr_2Cu]^{6+}$ are kept frozen. The open-shell character of the Cu ion would mean that a partially occupied orbital, the Cu-$3d(x^2\text{-}y^2)$, has to be kept frozen, a feature which is not yet implemented in our programs. Instead calculations are done with a frozen charge distribution of a Mg^{2+} ion. The divalent magnesium ion has an effective ionic radius that is virtually equal to that of Cu^{2+}: 0.86 Å vs 0.87 Å for a sixfold coordination and 0.71 Å for both in case of a fourfold coordination.[70] The wave function of the frozen fragments is expressed in a minimal basis set for the ions, i.e., $(13s,10p,4d)/[4s,3p,1d]$ for Sr^{2+} (Ref. 71) and $(13s,8p)/[2s,1p]$ for Mg^{2+}.[69]

Table III gives the results of the CASCI, MP2-2, DDCI2, and DDCI3 calculations for leg and rung. These numbers clearly show that the ratio between $J_\perp$ and $J_\parallel$ does not show a very strong dependence of the computational scheme applied; all of them indicate a slightly smaller magnetic interaction for the rung than for the leg. However, as known from previous studies, the absolute values of the calculated *J*'s differ strongly between one method and the other. We observe a relative small antiferromagnetic interaction in the CASCI calculations, which is greatly enhanced by the inclusion of external electron correlation (MP2-2, DDCI2, or DDCI3). The fact that MP2-2 and DDCI2 cause an enlargement of *J* by a factor of 3 has been observed before in many other compounds, e.g., La_2CuO_4 and NiO, but the doubling of *J* by adding the determinants connected to a relaxation of the charge-transfer excitations to the wave function (DDCI3) is significantly larger than has been observed for La_2CuO_4, for which an increase of about 40% has been observed.[49] This indicates that covalent interactions are relatively more important in $SrCu_2O_3$, which is also expressed in the values of *J* obtained with DDCI3, which are about 25% larger than in La_2CuO_4. Our final and most reliable *ab initio* estimates for $J_\perp$ and $J_\parallel$ are −139.3 and −155.8 meV, and hence, the ratio of both parameters equals 0.9.

Finally, we consider a different type of magnetic interaction in $SrCu_2O_3$ arising from the interaction of the spin moments on Cu ions located on the legs of different ladders. This interaction is assumed to be very weak because it involves an interaction in which the two O-$2p$ orbitals which participate are orthogonal to each other. The explicit calculation of the magnitude of this interaction can be done in a Cu_2O_6 cluster and indeed yields a very small and ferromag-

netic interaction of 0.95 meV at the CASCI level; i.e., the computational details are those of the Cu_4O_{10} cluster and hence, external electron correlation is not accounted for in the present estimate. However, the inclusion of these external electron correlation effects through DDCI3 increases the calculated magnitude of J_{inter} up to 12.5 meV (see Table III). This is an unexpected result, the interladder interaction is now ~10% of the magnetic interactions along the legs and rungs. This interaction may need to be considered in the fitting of experimental data, and the assumption of isolated two-leg ladders in $SrCu_2O_3$ reconsidered.

V. SUMMARY AND CONCLUSIONS

We have calculated *ab initio* estimates of $J_\perp$, $J_\parallel$, and J_{inter} of the ladder compound $SrCu_2O_3$. The material has been represented by small clusters that contain the essential ions involved in the superexchange processes. The clusters are embedded in a background of point charges that account for the long-range electrostatic interactions (the Madelung potential) and in addition we have included the short-range Pauli repulsion to prevent an artificial polarization of the cluster charge distribution towards the point charges. Within this material model we obtain accurate approximations of the quantities determining the magnetic coupling constants with quantum chemical and density functional techniques. The simple CASCI and UHF approximations result in antiferromagnetic but relatively small magnetic coupling parameters for leg and rung. The values are greatly enlarged by incorporating external electron correlation effects in the *N*-electron wave function. While the absolute magnitudes of the coupling parameters change dramatically with electron correlation, the ratio is fairly stable of $J_\perp/J_\parallel \approx 0.9$.

Beside the dependency of $J_\perp$ and $J_\parallel$ on the choice of the one-electron space and the details of the representation of the short-range repulsion, we have also investigated how the magnetic interactions along the rung and the leg interfere with one another. By comparing the *J* values extracted from a Cu_4O_{10} cluster which contains both superexchange paths along the leg and along the rung with those obtained from the two-center clusters, we can conclude that the two superexchange processes are completely independent. The parameters differ by less than 1% in the two-center and the four-center clusters. In addition we have calculated the interchain coupling by constructing a cluster with two Cu ions from different legs. As expected, this interaction turns out to be ferromagnetic, but its magnitude is significantly larger than generally assumed.

Our final and most reliable *ab initio* estimates of $J_\perp$ and $J_\parallel$ are -139.3 and -155.8 meV respectively, as listed in Table III. These values lead to a ratio of 0.9. Although the values of $J_\perp$ and $J_\parallel$ are very reasonable in comparison with the experimental and semiempirical estimates reported in the early literature, the ratio is in sharp contrast to the most recent determinations by Johnston *et al.*,[22] Eccleston *et al.*,[26] and Imai *et al.*[27] Their interpretation of the experiments suggest that $J_\perp$ is only half of $J_\parallel$. As put forward by Eccleston, this is a rather surprising finding since the Cu—O—Cu links for leg and rung are very similar. In the Introduction we have discussed the differences between these two bonds and none of these can be the origin of such a large difference in magnetic coupling along the leg and the rung. In fact, the difference in bond length favors the magnetic interaction along the rung, since this bond is slightly shorter. The exact effect of the difference in local geometry for the two bonds is not easily quantized. The effect of the local geometry is threefold, first it contributes to the differences in the Madelung potential between the oxygen on the rung and the oxygen on the leg; secondly, it introduces a different Pauli repulsion between the cluster ions and the environment; and in the third place it polarizes the oxygen anions on the leg and the rung in a different manner. The second point is not essential since the ratio of 0.9 is also observed for an embedding with point charges only, i.e., the Pauli repulsion causes an approximately equal increase of *J* for leg and rung. Although *J* is susceptible to changes in V_{MAD}, the dependency is rather weak[36] and actually, the difference affects the parameters in the opposite direction because *J* increases for a reduction of the Madelung potential.[36,72] Therefore, the most likely origin of the ratio of 0.9 encountered in our calculations is the different polarization of the Cu—O—Cu bonds by the ions in the direct neighborhood of the Cu_2O_7 clusters for leg and rung. Note that this polarization effect is also present in the clusters in which no Pauli repulsion (i.e., an embedding of point charges only) is included between the cluster ions and the surrounding centers, consistent with our findings that the ratio $J_\perp/J_\parallel$ does not depend on the exact details of the representation of the cluster surroundings. In addition, we have shown that the superexchange processes along rung and leg do not interfere and cannot cause $J_\perp$ to be half of $J_\parallel$.

Finally, we discuss our results in terms of the well-known *t*-*J* model Hamiltonian, which can be derived from the Hubbard model Hamiltonian by a perturbation expansion in t/U. In the *t*-*J* model, *J* is proportional to t^2/U, where *t* is an effective Cu-Cu hopping integral and *U* is the effective on-site two-electron Coulomb repulsion integral. We see no reason to doubt that all Cu sites exhibit roughly equal *U* (within 10% or so). The origin of the anisotropy would then appear to lie exclusively in the influence of the oxygen centers on the effective hopping parameter *t*. The ratio would suggest that *t* along the rung should be smaller than *t* for the leg. However, the explicit calculation of *t* for leg and rung indicates that this parameter is (as might have been expected) larger for the shorter distance (i.e., for the rung). We conclude that the observed anisotropy cannot be explained within a simple *t*-*J* model.

We have also found that the assumption of a weak interladder coupling is not supported by our calculations, and hence, this magnetic interaction cannot be excluded as a possible source of large anisotropy within the ladder. We must point out that the DDCI3 calculated value for $J_\parallel$ is in excellent agreement with the experimental estimate whereas a fairly large discrepancy is found for $J_\perp$. However, the fact that a significant J_{inter} coupling is found means that the measured $J_\perp$ is in fact an effective magnetic coupling parameter for the two magnetic interactions. Notice that the appearance of J_{inter} introduces spin frustrations in the systems that may play a role in the experimental determination of the $J_\perp/J_\parallel$ ratio.

In summary, the two-leg ladder material $SrCu_2O_3$ represents a very challenging case. We have not found a simple explanation for the experimentally observed strong anisot-

ropy. While the present *ab initio* cluster model calculations yield a qualitatively correct anisotropy, in the sense that J along the leg is larger than J for the rung, they predict a fairly small anisotropy and fail to predict the experimentally observed ratio of about 1/2. We examined a number of possible sources of this discrepancy and found a significant value for the interladder interaction that is not taken into account in the models used to fit experimental data to extract the magnetic coupling constants. This may possibly play a role in resolving the discrepancy between the *ab initio* calculated values and the experimental estimates.

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