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Magnetic interactions in calcium and sodium ladder vanadates

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Magnetic interactions in ladder vanadates are determined with quantum chemical computational schemes using the embedded cluster model approach to represent the material. The available experimental data for calcium vanadate is accurately reproduced and the nature of the interladder interaction is established to be ferromagnetic. An analysis of the main contributions to the magnetic couplings is presented and the role of the covalently bonded apex oxygen is elucidated. In the sodium vanadate, the ground state configuration of the rungs is $V-3d^1-O-2p^5-V-3d^1$. We show that with this configuration good intrachain coupling constants are obtained for the high-temperature phase. The interchain coupling in NaV_2O_5 is predicted to be ≈ 34 K, ferromagnetic in nature.

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I. INTRODUCTION

Interactions between localized spin moments in transition metal (TM) materials are a source of fascinating phenomena. Examples are the strong antiferromagnetism in the parent compounds of the high-temperature superconductors, the spin-Peierls dimerization in $CuGeO_3$, and the spin-gap behavior in low-dimensional copper and vanadium oxides.

Many of the magnetic properties of such spin systems can be understood in terms of Heisenberg Hamiltonian models with predominantly nearest-neighbor coupling. Over the last years *ab initio* quantum chemical methods based on embedded cluster models proved to be valuable tools not only to accurately predict the magnitude of the magnetic coupling parameters, but also to elucidate the underlying microscopic mechanisms. Within such an approach, the coupling constants can be derived from the energy eigenvalues of the states arising from different spin configurations by mapping spin eigenfunctions of the N -electron cluster Hamiltonian onto the Heisenberg Hamiltonian. The magnetic coupling J for a cluster with two $S=1$ centers is extracted either from the singlet–triplet or the singlet–quintet splitting:^{1,2} $E_S - E_T = J$, $E_S - E_Q = 3J$.

Most of the TM insulators exhibit antiferromagnetic (AFM) order. The antiferromagnetism is qualitatively explained by the Anderson super-exchange mechanism,³ which involves electronic excitations from one magnetic center to the other via the intervening ligand. In a cluster model approach this effect can be accounted for by complete active space configuration interaction (CASCI) schemes where the active space includes the open-shell TM orbitals. Such active space contains the ground state configuration formed by the so-called neutral determinants and all metal to metal charge transfer (CT) configurations formed by the ionic determinants. Calculations at this level of accuracy usually repro-

duce the sign of the interaction, but the magnitude of the coupling parameter is severely underestimated. Various methods have been developed to include effects that go beyond the CASCI approximation. By gradually improving the description of the cluster wave function, detailed information about the physical mechanisms determining J can be obtained.

A procedure successfully applied for the study of magnetic couplings in an extensive series of materials is difference dedicated configuration interaction (DDCI).^{4,5} The states defining J are expressed in terms of CI expansions including single and double excitations from a CAS formed by the open-shell orbitals. The CI expansion is however restricted by eliminating all the double excitations from inactive to virtual orbitals, i.e., those that do not involve any of the open-shell orbitals. In second-order perturbation theory, these determinants only cause a shift in the diagonal matrix elements of the CI matrix and hence do not contribute to the energy difference of the states of interest. We will refer to this scheme as DDCI.

Second-order perturbation theory indicates that for a strictly degenerate reference wave function, the CI expansion can be further reduced without loss of accuracy by also eliminating the excitations that involve just one open-shell orbital. This scheme, referred to as DDCI2, takes into account the second-order terms discussed by de Loth *et al.*⁶ and normally yields 50–80 % of the experimental J .^{7–11} It has been shown that the remaining difference with experiment can be recovered at the DDCI level.^{8–12} The difference between DDCI2 and DDCI has been attributed to a more effective relaxation of the metal to metal and the ligand to metal CT configurations.^{9,13}

The effect of orbital relaxation in the CT component of the wave function has been investigated by van Oosten *et al.*^{14,15} in several AFM cuprates by means of nonorthogonal CI (NOCI).¹⁶ These calculations were based on small CI expansions including only $O \rightarrow TM$ excitations, where both

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the reference and the CT excited states are expressed in their own optimized orbitals. It has been found that the AFM exchange is strongly enhanced by admixing relaxed CT states, with estimates for the coupling constants in close agreement with the experimental values, although somewhat smaller than the DDCI results.

The NOCI expansion is much shorter than for a conventional CI and offers an insightful chemical picture of such CT effects. However, the optimization of the excited states is often rather tedious. An approach which avoids both the optimization problems encountered in nonorthogonal CI and the relatively high computational demand of DDCI is based on the complete active space second-order perturbation theory (CASPT2) method developed by Andersson *et al.*^{17,18} CASPT2 starts from a complete active space self-consistent-field^{19,20} (CASSCF) reference wave function and approximates the remaining correlation effects by second-order perturbation theory. Recent studies^{21–23} have established that it gives accurate estimates of the magnetic coupling parameters for several Ni and Cu ionic compounds. It has been found that 90–95 % of the experimental J is recovered provided that the CASSCF reference wave function is supplied with enough flexibility to account for the relaxation of the CT configurations.²³

II. LADDER VANADATES

In this paper we apply the CASSCF/CASPT2 method to investigate the magnetic coupling parameters in vanadium oxides, namely the layered compounds CaV_2O_5 and NaV_2O_5 . Both materials have attracted considerable attention in the last years. CaV_2O_5 shows AFM order and a large gap in the spin excitation spectrum.^{24–26} In NaV_2O_5 an unusual phase transition has been observed at $T_c \approx 35$ K,²⁷ coupled with a lattice distortion,^{28–30} spin-gap formation,^{28–30} and charge ordering within the vanadium layers.^{31–35} Several studies, including studies based on *ab initio* wave function approaches^{36,37} and density functional theory (DFT) band calculations within the local density+ U approximation (LDA+ U)³⁸ addressed the low-temperature (LT) phase of NaV_2O_5 . The present study of the sodium vanadate is focused on the high-temperature (HT) phase.

CaV_2O_5 and NaV_2O_5 have similar crystal structures: the V ions, each roughly situated in the center of a pyramid of five oxygens, form layers in which one-dimensional (1D) vanadium chains are arranged in a network of two-leg ladders; see Fig. 1. The rungs are composed of two V ions connected by an oxygen. Within the same ladder, the VO_5 pyramids share the corners of their bases, whereas pyramids on adjacent ladders are linked by common edges and point alternately up and down with respect to the basal plane. In addition, pyramids on the same rung are tilted towards the bridging oxygen.

The ladder systems became subject of intense study when Dagotto *et al.*³⁹ and Barnes *et al.*⁴⁰ found evidence that the isolated AFM Heisenberg ladder has a finite spin gap. This system is the standard $S=1/2$ Heisenberg model on a ladder of two coupled spin chains, with couplings across the rungs, $J_\perp$, and along the legs of the ladder, $J_\parallel$. By using analytical and numerical techniques, the authors of Refs. 39

FIG. 1. Arrangement of the VO_5 pyramids in CaV_2O_5 and NaV_2O_5 . Two adjacent ladders are shown.

and 40 determined that a nonzero energy gap exists between the spin-singlet ground state and the spin-triplet excited states. Various experiments^{24–26} clearly indicate a singlet ground state and the existence of a large spin gap in CaV_2O_5 . Miyahara *et al.*⁴¹ have performed quantum Monte Carlo (QMC) simulations and shown that in CaV_2O_5 the temperature dependence of the magnetic susceptibility ($\chi(T)$) and the spin gap are well described by a trellis lattice Heisenberg model of weakly coupled $S=1/2$ spin ladders.

While in CaV_2O_5 one spin is attached to each vanadium site, in NaV_2O_5 the character of the electronic ground state is less obvious. X-ray diffraction^{42–45} and nuclear magnetic resonance (NMR) measurements⁴⁶ have shown that above T_c all V ions are crystallographically equivalent. The resulting formal charge of +4.5 suggests that one d electron is shared by two vanadium ions on the same rung. This model leads to a magnetic structure of quasi-1D AFM spin chains with a spin of 1/2 per rung of the ladder.^{45,47} Recently, a modification of this picture has been proposed in which the rung ground state is characterized by a $\text{V}-3d_{xy}^1-\text{O}-2p_y^1-\text{V}-3d_{xy}^1$ configuration.⁴⁸ The three unpaired electrons are spin coupled to a doublet and give rise to an effective spin of 1/2 per rung, just as in the conventional model for the ground state of NaV_2O_5 and the experimental evidence for the quasi-1D spin chain character of the compound. The important role of the $\text{V}-3d_{xy}^1-\text{O}-2p_y^1-\text{V}-3d_{xy}^1$ configuration in the rung ground state was already recognized by Suaud and Lepetit,^{37,49} who found an almost equal weight for the configurations with one d -electron shared by two vanadiums and the configuration with an unpaired electron on the bridging oxygen.

By analyzing the magnetic contribution in the Raman spectrum, the exchange across the rung of the ladder was estimated in CaV_2O_5 to be $J_\perp \approx -640$ K, about ten times larger than the interaction along the leg, $J_\parallel$.²⁶ The QMC simulations of Miyahara and co-workers⁴¹ reproduce the experimental $\chi(T)$ curve with two sets of parameters. Assuming a ferromagnetic (FM) interladder interaction, values are obtained that are rather similar to the LDA+ U calculations of Korotin *et al.*⁵⁰ (see Table I). However, an equally good agreement was obtained by restricting the interladder inter-

TABLE I. Experimental and calculated magnetic coupling parameters in CaV_2O_5 . Negative coupling denotes AF exchange.

$J_{\perp}$ (K)	$J_{\parallel}$ (K)	J' (K)	Method
−640	−64	−	Raman scattering ^a
−670	−67	−45	$\chi(T)$ ^b
−665	−135	25	$\chi(T)$ ^b
−608	−122	28	LDA+ U^c
−730	−587	−170	Extended Hückel ^d

^aReference 26.^cReference 50.^bReference 41.^dReference 51.

action to negative, i.e., AFM, values. The comparison of the experimental data listed in Table I shows that the nature and magnitude of the magnetic coupling along the rungs is well established, but the other two couplings are less clear.

In NaV_2O_5 the AFM coupling along the quasi-1D spin chain inferred from $\chi(T)$ data is between −529 and −560 K for the HT phase.^{27,52} The reported HT theoretical estimates are spread over a wide range, from approximately −900 K by DFT and model Hamiltonian studies to about −30 K by embedded cluster CI calculations. Rather different values have been found for the interchain coupling J' as well (see Table II).

III. COMPUTATIONAL INFORMATION

We have used three different bi-pyramidal clusters to determine the Heisenberg magnetic couplings in CaV_2O_5 : a $[\text{V}_2\text{O}_9]^{10-}$ cluster with two V ions on the same rung for $J_{\perp}$, a $[\text{V}_2\text{O}_9]^{10-}$ fragment with two adjacent magnetic centers on the same leg of a ladder for $J_{\parallel}$, and $[\text{V}_2\text{O}_8]^{8-}$, including two edge-sharing VO_5 pyramids, for the interladder coupling J' . Each of these parameters has been obtained as the energy difference between the singlet and the triplet electronic states, $J = E_S - E_T$. Larger $[\text{V}_4\text{O}_{16}]^{14-}$ clusters that include two V–O–V rungs have been employed to calculate the intrachain and interchain coupling for NaV_2O_5 . This is a necessary strategy since the whole V–O–V rung must be con-

sidered as a magnetic unit. The magnetic couplings along the quasi-1D spin chain and between adjacent chains are again derived from the energy eigenvalues of the singlet and triplet states.

All-electron CASSCF/CASPT2 calculations have been performed with the MOLCAS 5 program package.⁵⁵ Two types of CASSCF wave functions are constructed. First, we only include the magnetic orbitals in the active space, i.e., two V-3*d* orbitals for CaV_2O_5 and four V-3*d* plus two O-2*p* orbitals for NaV_2O_5 , with two and six active electrons, respectively. This active space will be referred to as minimal CAS. Second, we extend these active spaces with oxygen 2*p* orbitals involved in the magnetic interaction, plus a set of virtuals, the so-called prime orbitals, to account for dynamical (or atomic) correlation effects among the active electrons. Since there is at most one *d* electron per vanadium site in the compounds studied here, this dynamical correlation should not be important at the vanadium sites.⁵⁶ Therefore, only O-2*p* correlating orbitals (the so-called O-2*p'* orbitals) are included in this extended active space, which will be referred to as extended CAS. The number of orbitals and electrons in this extended CAS differs from case to case and will be specified when discussing the results of these calculations.

The subsequent CASPT2 step estimates the remaining part of electron correlation within the valence V-3*d* and O-2*p*, and correlation effects due to the semicore V-3*s*, 3*p* and O-2*s* electrons. The CASPT2 calculations based on the minimal active space neglects the coupling between configurations external to this CAS. However, the extension of the active space with oxygen 2*p* orbitals introduces the major part of these couplings in the calculation. As demonstrated in Refs. 21–23, such CASSCF/CASPT2 calculations ensure an accurate treatment of both electron correlation and relaxation effects connected with TM-3*d* to TM-3*d* CT and ligand-2*p* to TM-3*d* CT excitations.

For CaV_2O_5 , the CASPT2 results are compared to DDCI calculations. These calculations have been performed with the CASDI code.⁵⁷ Singlet–triplet average natural orbitals have been used as molecular orbital basis to construct the Slater determinants in the CI, following the iterative DDCI (IDDCI) scheme proposed in Ref. 58. In the case of NaV_2O_5 the full DDCI expansion becomes prohibitively large and therefore we compare the CASPT2 results with the more approximate IDDCI2 scheme. Realizing that this type of approximation reproduces 50–80 % of the experimental value, the comparison can validate the sign and the order of magnitude of the interactions derived from the CASPT2 calculations.

The clusters described above are embedded in arrays of PCs that reproduce the crystal Madelung potential. Following the conclusions of previous calculations,^{37,48,49,59} we use charges for the vanadium, and the apex and rung oxygen centers that are smaller than the formal ionic charges. It is by now well established that in NaV_2O_5 the apical oxygen O_A is bonded to the vanadium atom by a slightly polarized double bond and presents only a charge of approximately $-1.0e$. This picture is supported by Raman scattering (RS)

TABLE II. Experimental and calculated high-temperature magnetic couplings in NaV_2O_5 . Negative coupling denotes AF exchange.

$J_{\parallel}$ (K)	J' (K)	Method
−560		$\chi(T)$ ^a
−529		$\chi(T)$ ^b
−928		DFT ^c
−870	−151	Hubbard model ^d
−600		DFT ^c
−29	14	DDCI ^f
	−12	Bond-operator study ^g
−530		Extended Hückel ^h

^aReference 27.^bReference 52.^cReference 45.^dReference 47.^eReference 53.^fReference 49. These values are obtained by dividing $J_{\parallel}$ and J' listed in Table I of Ref. 49 by 2 and 4, following the indications of the authors at the end of Sec. III.^gReference 54.^hReference 51.

TABLE III. Magnetic coupling parameters (in K) for CaV_2O_5 by CASSCF/CASPT2 and IDDCI calculations on bi-pyramidal clusters. Values in parentheses correspond to results with larger atomic basis sets: V ($6s5p4d2f$), O_{bridge} ($4s3p2d$), O_{edge} ($4s, 3p$).

	CASSCF	CASPT2	IDDCI
(1) Minimal CAS			
$J_{\perp}$	-208 (-210)	-676 (-672)	-671 (-676)
$J_{\parallel}$	-36 (-37)	-113 (-109)	-55 (-59)
J'	46 (44)	49 (43)	114 (107)
$J_{\parallel}/J_{\perp}$	0.17 (0.18)	0.17 (0.16)	0.08 (0.09)
(2) Extended CAS			
$J_{\perp}$	-195 (-196)	-678 (-676)	-701
$J_{\parallel}$	-37 (-39)	-106 (-107)	-60
J'	22 (18)	36 (29)	94
$J_{\parallel}/J_{\perp}$	0.19 (0.20)	0.16 (0.16)	0.09

measurements,⁶⁰ where several lines of the spectrum are interpreted in terms of vibration modes of the V–O_A group. Our Mulliken population analysis also confirms this picture: the charge of O_A is about $-1.0e$ in both vanadates. Therefore we represent Ca and Na by their formal charges, $+2.0e$, and $+1.0e$, respectively, whereas V is modeled in both materials by $+3.0e$ charges. The apical oxygens are represented by $-1.0e$ PCs and we assign also $-1.0e$ PCs to the rung oxygen O_R in NaV_2O_5 . The other oxygen centers (the oxygens on the leg, and the rung oxygen in CaV_2O_5) are modeled with their formal ionic charge of $-2.0e$. At the boundaries of each of these arrays, we place a set of charges optimized to fit the Madelung potential produced by the above-mentioned charges in the cluster region.

To avoid an artificial polarization of the cluster orbitals towards the neighboring positive PCs, the nearest vanadium, calcium, and sodium cations are described by TIPs.^{61,62} Atomic natural orbital (ANO) Gaussian-type basis sets have been applied: V ($21s15p10d6f$)/($5s4p3d1f$) for vanadium, O ($14s9p4d$)/($4s3p1d$) for the bridging and the apex oxygens, and O ($14s9p$)/($4s3p$) for the other oxygens in the clusters.^{63,64} For the clusters with four vanadiums we eliminated the f function on the vanadium and reduced the basis of the edge oxygens to ($3s2p$) to reduce the computational cost. We have used crystal structures as determined experimentally by Onoda and Nishiguchi²⁴ for CaV_2O_5 , and Meetsma *et al.*⁴² for NaV_2O_5 .

IV. RESULTS

A. CaV_2O_5

LDA+ U calculations⁵⁰ and NMR measurements⁴⁶ have shown that the unpaired d electron of a V ion occupies the xy orbital, where the x and y directions are, respectively, along the a and b axes of the $Pmmn$ reference system. The intraladder AFM interactions occur between V sites in corner-sharing VO₅ pyramids through the π -overlap of V- $3d$ and O- $2p$ orbitals. The V–O distance across the rung is shorter than along the leg, suggesting a stronger V- $3d$ –O- $2p$ coupling across the rung. Also the tilt of the VO₅ pyramids increases the $3d_{xy}$ – $2p_y$ overlap across the rung.

The results listed in Table III confirm that the major

coupling in CaV_2O_5 takes place across the rung. As previously observed for AFM interactions in other TM ionic compounds,^{21,23} the CASPT2 results are about three times larger than the CASSCF values obtained with the minimal CAS. The CASPT2 on-rung magnetic coupling, about -670 K, is in good agreement with the IDDCI result and with fits of both RS spectra²⁶ and $\chi(T)$.⁴¹ By symmetry, only the O- $2p_y$ can directly participate in the magnetic interaction. Adding this orbital and its correlating counterpart to the active space, gives an almost identical on-rung coupling.

The coupling along the leg is also AFM, but much weaker. The $J_{\parallel}/J_{\perp}$ ratio, 0.17, is between 0.10, deduced from RS data,²⁶ and 0.20, found by QMC simulations⁴¹ and LDA+ U calculations.⁵⁰ Due to the lower point group symmetry of the cluster representing the leg, C_s (versus C_{2v} for the rung cluster), all three $2p$ orbitals of the bridging oxygens can contribute to the coupling. Hence, the extended CAS now contains eight electrons and eight active orbitals. Nevertheless, essentially identical results are obtained as with the minimal CAS.

Different from the intraladder interactions, our calculations indicate that the coupling between V ions located on the legs of adjacent ladders is FM. This interladder interaction involves V–O–V bond angles of about 100° and little overlap, since the TM ions are on different sides of the basal plane. The minimal CAS, which includes the two $3d$ magnetic orbitals only, results in a coupling of about 45 K, with very small difference between the CASPT2 and the CASSCF estimates. As for the leg interaction, all three O- $2p$ orbitals can contribute to the magnetic interaction. Since the interaction between vanadiums on different ladders is bridged by two oxygen ligands, six O- $2p$ and six O- $2p'$ orbitals are added to the active space, resulting in a 14 orbitals, 14 electrons CAS. This extended CAS calculations preserves the picture of FM interladder interactions, although it slightly weakens the interaction to $J' = 36$ K. The CASPT2 J -values establish the fit of $\chi(T)$ where a FM J' was assumed (third entry in Table I) as the most realistic one.

The on-rung CASPT2 and IDDCI estimates are in good agreement. This is, however, not so obvious for the other two magnetic couplings, for which a difference of about 50 K is observed. Such (relatively) large differences, about the same size as the coupling itself in case of J' , have not been observed in the comparison of the two methods by de Graaf and co-workers,²³ and need a closer look. We analyze this difference in two steps: First, we have decomposed the CASPT2 contribution to the magnetic coupling and second, we have performed IDDCI calculations with an extended CAS.

B. Decomposition of J

Table IV lists the contributions of the different type of excited configurations to the total CASPT2 J values obtained with the larger atomic basis set specified in the caption of Table III. The different contributions are ordered following the number of electrons removed from the inactive orbitals (h for holes) and/or electrons promoted to the virtual orbitals (p for particles) with respect to the configurations in the

TABLE IV. Differential contributions (in K) to the magnetic coupling constant in CaV_2O_5 of the different type of configurations. The minimal CAS contains the ground state and all V to V CT configurations, h indicates the creation of a hole in the inactive orbitals, and p the creation of a particle in the virtual orbitals.

Excitation type	$J_{\perp}$	$J_{\parallel}$	J'
Minimal CAS	-210	-37	44
$1h$	0	0	0
$2h$	-36	-6	-5
$1p$	0	0	0
$1h-1p$	-396	-81	-44
$2h-1p$	-130	2	53
$2p$	-16	-3	-1
$1h-2p$	108	26	29
$2h-2p$	9	-8	-33
Total PT2	-462	-72	-1
Total	-672	-109	43

minimal CAS. For example, in the $2h-1p$ configurations, two electrons are taken out of the inactive space, one is promoted to the virtual orbitals and the other is placed in an active orbital.

Since the orbitals are optimized for both the singlet and the triplet state, the $1h$ and $1p$ configurations do not contribute because of Brillouin's theorem (see Table IV). The $1h-1p$ configurations contribute to the spin-polarization and the relaxation of the ionic configurations, $\text{V-}3d^0-\text{O-}2p^6-\text{V-}3d^2$. The latter effect can also be understood as a screening of the on-site repulsion U . At this stage we cannot distinguish between the two mechanisms but the relaxation of the ionic configurations is expected to be dominant.¹³ This relaxation or screening of U increases the kinetic exchange (t^2/U) and hence favors the singlet state. The overall effect of these configurations is large in the three couplings present in CaV_2O_5 and for the AFM on-rung and leg magnetic coupling they are even the dominant terms. The $2p$ and $2h$ configurations give AFM contributions but are relatively small, in agreement with the analysis in Ref. 13. The $2h-1p$ and $1h-2p$ configurations account for the contribution to the kinetic exchange of the ligand to metal CT configurations. Their contributions are important, although they almost cancel for the rung interaction.

Finally, we focus attention on the $2h-2p$ configurations, whose contributions are strictly zero in case of a common orbital part for the singlet and triplet wave function. We find however nonzero values because we apply separately optimized orbitals for the two states. Whereas the total contribution of these excitations constitutes about 90% of the second-order energy correction, its differential effect is very small for $J_{\perp}$. The differential effect is somewhat larger for $J_{\parallel}$ and absolutely indispensable for J' . Since these $2h-2p$ contributions are not included in the IDDCI scheme, they may be invoked to explain the differences observed between the CASPT2 and IDDCI results in Table III. Adding the $2h-2p$ contributions to the IDDCI J values, brings the two sets of calculations in better agreement. Such large contributions of the $2h-2p$ configurations are not observed for the largely ionic copper oxide compounds La_2CuO_4 and SrCu_2O_3 . This suggests that the ladder vanadates present a special case,

possibly due to the presence of the covalently bound apex oxygen.

This assumption is supported by the finding that the $2h-2p$ contribution is smaller when the orbitals associated with the covalent V-O_A bond are left out of the correlation treatment. The most pronounced change is found for the interladder interaction, precisely where the contribution is largest. The $2h-2p$ excitations only contribute -17 K when the O_A are kept frozen in the CASPT2, to be compared with -33 K for the complete calculation. The reduction is less dramatic for $J_{\parallel}$, the $2h-2p$ contribution is -5 K. By subtracting the CASPT2 value obtained with the frozen V-O_A bond from the complete calculation, we also can establish the overall contribution of O_A , which turns out to be significant and AFM in all three cases, -140 K for $J_{\perp}$, -23 K for $J_{\parallel}$, and -5 K for J' .

C. Comparison with IDDCI

The $2h-2p$ configurations can (at least partly) be included in the IDDCI treatment by extending the active space with formerly doubly occupied orbitals. In the present case, the extended CAS contains the magnetic orbitals and the two occupied orbitals that most contribute to the magnetic coupling,⁶⁵ which turn out to be located on the bridging oxygens. Hence, concerning the introduction of the $2h-2p$ configurations, this extension of the active space only introduces the configurations connected to the bridging atoms. In a recent paper, this strategy has been employed in the description of the electronic structure of a binuclear copper complex in which the Cu^{2+} ions are connected by two azido bridges.⁶⁶ The extension of the active space has a dramatic effect on the FM interaction, showing an important role of the $2h-2p$ excitations on the azido bridges in this complex.⁶⁷

For the magnetic coupling parameters in CaV_2O_5 , the extension of the active space only has a moderate effect; see Table III. All interactions turn out to be somewhat more AFM. The relative changes are 4.5%, 9.0%, and 17.5% for $J_{\perp}$, $J_{\parallel}$, and J' . The relative largest change observed for J' is in accordance with the CASPT2 results, which also show the largest contribution of the $2h-2p$ configurations for this coupling. Recalling that the CASPT2 analysis also indicates a non-negligible contribution of $2h-2p$ excitations connected with other atoms (e.g., the apex oxygens), it can be argued that a further extension of the active space in the IDDCI calculation would result in a further lowering of J' , which would bring the two computational approaches in better agreement.

D. NaV_2O_5

Table V lists the results of the calculations carried out on V_4O_{16} clusters composed of two V-O-V rungs to extract CASSCF/CASPT2 estimates for the intrachain ($J_{\parallel}$) and interchain (J') magnetic couplings. The minimal CAS, which includes four $\text{V-}3d_{xy}$ orbitals and two $2p_y$ orbitals of the oxygen on the rung, predicts a rather weak AFM interaction along the chain and a FM interchain coupling. In the subsequent CASPT2 calculations, serious intruder state problems appear. As any perturbational scheme based on a monoelec-

TABLE V. High temperature magnetic couplings (in K) for NaV_2O_5 by CASSCF/CASPT2 calculations using a V_4O_{16} cluster.

	CASSCF	CASPT2 ^a	IDDCI2
(1) Minimal CAS			
$J_{\parallel}$	-90	-326 ± 39	-398
J'	26	34 ± 6	18
(2) Extended CAS			
$J_{\parallel}$	-111	-559 ± 44	
J'			

^aLevel shifts between 0.20 and 0.32 Hartree have been applied.

tronic $\hat{H}^{(0)}$, there can be configurations with expectation values of $\hat{H}^{(0)}$ that are very close to (or even smaller than) the expectation value of the configurations in the reference wave function. This causes a breakdown of the perturbational treatment.

To overcome these intruder state problems, we have applied the level shift technique proposed by Roos and Andersson.⁶⁸ All configuration external to the CAS are shifted in energy by an arbitrary amount to avoid near degeneracies. Estimates of J can be obtained without the interference of intruder states after correcting the resulting second-order energy for the level shift. The price to pay is that J shows a modest dependency on the level shift applied and some degree of uncertainty is contained in the results. The interval of level shifts applied, from 0.20 to 0.32 Hartree, is a compromise between shifting away all intruder states and keeping the error of the level shift correction as small as possible. In this interval $J_{\parallel}$ varies between -287 and -365 K and J' between 29 and 41 K.

When extending the CAS, for the same range of level shifts, we observe an enhancement of the absolute value of the intrachain coupling by approximately 200 K. Because the active vanadium d orbitals, essentially of d_{xy} character, exhibit some admixture of the d_{yz} components, we introduce into the active orbital set not only the $2p_x$, but also the $2p_z$ levels (plus the corresponding correlating virtuals) of the oxygen ions located on the legs of the ladder between the two rungs. This extended CAS contains 14 orbitals and 14 electrons. The large increase of the intrachain magnetic interaction proves the essential role of these oxygen $2p$ orbitals in connecting magnetically adjacent rungs on the same ladder. Although some uncertainty is contained in our result, rather good agreement is found with the estimates of Refs. 27 and 52. The value of $J_{\parallel}$ is only weakly dependent on the choice of the point charges. Representing O_A by -0.5 and O_R by -2.0 , which corresponds to the choice of Suaud and Lepetit,^{37,49} we obtain -583 ± 44 K.

A well-balanced extension of the active space for the interchain interaction implies the addition of 12 orbitals to the active space (six $\text{O}-2p$ and six $\text{O}-2p'$; see the discussion of the results for CaV_2O_5). This results in an extended CAS of 18 orbitals with 18 electrons, which is beyond the possibilities of current computer resources. Therefore, our estimate for J' is that based on the minimal CAS ($34 \text{ K} \pm 6 \text{ K}$), although this number must be taken with some caution in light of the relatively large effect of adding the bridg-

ing orbitals to the active space in case of the intrachain coupling.

To give a more firm basis to the CASPT2 results obtained with the level shift technique, we compare them to IDDCI2 results. This is especially relevant for the interchain magnetic interaction, since no experimental data are available. The latter computational scheme is variational and hence is not plagued by the intruder state problem. IDDCI2 commonly reproduces the sign and the order of magnitude of the interaction. The last column in Table V shows that the IDDCI2 value of -398 K indeed corresponds to $\approx 70\%$ of the estimates derived from the magnetic susceptibility measurements. Extrapolating this finding to the interchain magnetic coupling, IDDCI2 confirms the FM nature of the J' found with CASPT2. Under the assumption that the IDDCI2 value of 18 K is between 50% and 70% of the real J' , the CASPT2 value of $34 \text{ K} \pm 6 \text{ K}$ can be considered to be of the right magnitude.

Finally, we want to stress that the differences between our IDDCI values and those of Suaud and Lepetit⁴⁹ is due to the different strategy applied by these authors to represent NaV_2O_5 and not to the computational scheme, which is basically the same except for some small computational details. The bi-pyramidal clusters used by Suaud and Lepetit to evaluate the magnetic couplings cannot account for the $\text{V}-3d^1-\text{O}-2p^5-\text{V}-3d^1$ character of the ground state in an explicit way.

V. CONCLUSIONS AND SUMMARY

The ladder structure of the calcium and sodium vanadates gives rise to different magnetic exchange pathways that couple the spin moments localized on the vanadium centers (CaV_2O_5) or $\text{V}-\text{O}-\text{V}$ rungs (NaV_2O_5). To study the relative magnitude of these interactions and get more insight in the mechanism of the coupling, we have performed *ab initio* quantum chemical calculations on embedded cluster models. For the calcium compound the experimental data are fairly well established, which permits us to validate our computational scheme. Nevertheless, there is some uncertainty about the magnitude of the interactions along the leg and the sign of it between the ladders. Our CASPT2 calculations give $J_{\perp} = -678$ K, in excellent agreement with the estimates derived from RS measurements and the $\chi(T)$ dependence. The other two exchange interactions are calculated to be $J_{\parallel} = -106$ K, and $J' = 36$ K.

The partitioning of the CASPT2 energy evidences the important role of the relaxation of the ionic determinants manifest in the large contribution of the $1h-1p$ excitations. Furthermore, we found important contributions of the $2h-1p$ and $1p-2h$ excitations. These excitations are connected to ligand to metal CT excitations. The contribution of the covalently bound O_A is AFM for all three couplings.

The rather complex electronic structure of NaV_2O_5 makes the determination of the magnetic couplings less straightforward. In the first place, the whole $\text{V}-\text{O}-\text{V}$ rung must be considered as magnetic unit. Therefore, we need relatively large cluster models with four vanadium centers. Second, the reference wave function must reflect the $\text{V}-3d^1-\text{O}-2p^5-\text{V}-3d^1$ character, which implies a minimal

active space of six orbitals with six electrons. Finally, the extension of the CAS with the $2p$ orbitals of the oxygens that bridge between the V–O–V rungs increases the coupling along the ladder with more than 200 K. After correcting for the appearance of intruder states, we obtain $J_{\parallel} = -560 \text{ K} \pm 44 \text{ K}$, in good agreement with experimental estimates and establish the interchain interaction J' to be FM and about 35 K.

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