Electronic structure and exchange coupling in α'-NaV_2O_5

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Band-structure calculations of the electronic structure of α'-NaV_2O_5 were performed using the linear muffin-tin orbital method within the local-density approximation (LDA). The results of the calculations were used to determine the parameters of an extended tight-binding model which describes the dispersion of the bands formed by V d_{xy} orbitals and includes explicitly V d_{xy}–O$p_{x,y}$ hopping terms. It has been found that the effective hopping between d_{xy} orbitals of V atoms placed at the opposite ends of consecutive rungs of a ladder is comparable to the hopping along the leg of the ladder, which suppresses the dispersion of the upper pair of V d_{xy} bands. The electronic structure of different models for the charge-ordered low-temperature phase of α'-NaV_2O_5 was studied using the LDA+U approach. The LDA+U ground-state energy was calculated and compared for in-line and zigzag charge order in different magnetic configurations. The set of effective exchange constants between V^{4+} magnetic moments was calculated by mapping to the ground-state energy of a localized Heisenberg model.

I. INTRODUCTION

Among other transition-metal oxides vanadates have recently attracted special attention due to the observation of the low-temperature behavior typical for ''heavy fermion'' compounds in LiV_2O_4 (Ref. 1) and a spin-Peierls- (SP-) like transition in α'-NaV_2O_5.[2] From the superstructure formation which gives rise to additional x-ray reflections at $\mathbf{q}=(\frac{1}{2},\frac{1}{2},\frac{1}{4})$ and a drop of the susceptibility below $T_c=33$ K it was concluded that α'-NaV_2O_5 is the second inorganic SP compound after $CuGeO_3$ (Ref. 3) with the highest transition temperature yet observed. In accordance with the original structure analysis[4] the existence of two sets of inequivalent $V^{5+}(S=0)$ and $V^{4+}(S=\frac{1}{2})$ sites already above T_c was assumed and the transition was supposed to be due to the singlet formation leading to a dimerization of spin-$\frac{1}{2}$ V^{4+} chains along the b axis.

Further investigations have shown, however, that the compound does not undergo a conventional SP transition. X-ray diffraction experiments[5,6] revealed that above T_c α'-NaV_2O_5 has a centrosymmetric *Pmmn* structure with one type of V site rather than a noncentrosymmetric $P2_1mn$ one as it was previously supposed. This implies that the high-temperature phase is a mixed valence compound and the average oxidation state of V ions is $V^{4.5+}$. Furthermore, only one set of equivalent magnetic V sites is observed in NMR measurements.[7,8] On the other hand, these experiments show that below T_c there exist two inequivalent V^{5+} and V^{4+} sites which can be explained by assuming that a charge ordering (CO) transition occurs in α'-NaV_2O_5. Thermal-expansion and specific-heat measurements[9] also provide evidence for two almost coincident phase transitions around T_c. The appearance of superimposed CO and SP transitions has been proposed within a theoretical model in Ref. 10.

Different models for the CO phase which account for spin gap formation have been proposed.[10–12] Although the low-temperature crystal structure is known by now[13] the associated CO model has not yet been determined unambiguously. The relevance of such a model can be verified by comparison of the calculated dispersion of magnetic excitations with the experimental one. Previous neutron scattering data[14] did not yet allow us to distinguish between different possibilities; more recent experiments with higher resolution[15] have improved this possibility.[16] The spin excitation spectra found in Ref. 15 were discussed in Ref. 17 and for the various proposed CO structures have been studied in detail in Ref. 16. It should be noted that the theoretical spectra are rather sensitive to the actual values of exchange constants and their reliable determination is a very important and challenging task.

It has been demonstrated recently for low carrier Yb_4As_3 (Ref. 18) that a comparison of the total energies calculated on the basis of the LDA+U approach can provide valuable information on a relative stability of different CO phases. The same approach can be applied to study the energy gain from the development of a particular kind of magnetic order within a given CO phase and to obtain realistic estimates for effective intersite exchange constants.

The paper is organized as follows. The theoretical approach and the computational details are explained in Sec. II.

Section III A presents the electronic structure of α'-NaV_2O_5 calculated in the local spin-density approximation (LSDA) approach and the tight-binding model constructed on the base of these calculations. The electronic structure calculated for different models of the CO phase using the LDA+U method is analyzed in Sec. III B while in Sec. III C the effective exchange coupling parameters between the V^{4+} magnetic moments are estimated. Finally, the results are summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

To analyze the details of the chemical bonding in α'-NaV_2O_5 we performed self-consistent band-structure calculations using the structural data for the high-temperature phase with the centrosymmetric *Pmmn* structure.[5] The structure consists of double chains of edge-sharing distorted VO_5 pyramids running along the orthorhombic b axis. In the ab plane V sites form ladders with legs and rungs parallel to b and a directions, respectively, with oxygen atoms placed at the rungs (O_R) and at the legs (O_L) of the ladder (cf. Fig. 3). The calculations were performed within the local-density approximation (LDA) to the density-functional theory using the linear-muffin-tin orbital (LMTO) method in the atomic-sphere approximation[19] (ASA) with the so-called combined correction term taken into account. The von Barth–Hedin parametrization for the exchange-correlation potential[20] has been employed. Application of the linear-muffin-tin orbital LMTO-ASA method to compounds like α'-NaV_2O_5 with an open layered structure can lead to erroneous results caused by a large overlap of space-filling atomic spheres (AS) surrounding each atom. The usual way to avoid this is to introduce additional ''empty'' spheres (ES) between the AS. For α'-NaV_2O_5 we inserted 12 ES into the simple orthorhombic unit cell which reduced significantly the sphere overlap. Test calculations showed that the band structure is not sensitive to the exact positions and radii of the ES as long as the overlap between the spheres is not too large. The Brillouin zone (BZ) integrations in the self-consistency loop were performed using the improved tetrahedron method[21] on a grid of 864 **k** points.

A realistic description of the electronic structure of the low-temperature phase cannot be obtained without accounting for strong electronic correlations at V sites. This can be at least partially achieved by using the LDA+U approach.[22] The LDA+U method is an efficient tool for calculating the electronic structure of systems where the Coulomb interaction is strong enough to cause localization of the electrons. It works not only for nearly corelike $4f$ orbitals of rare-earth ions, but also for transition-metal oxides, where $3d$ orbitals hybridize quite strongly with oxygen $2p$ orbitals (for a review see Ref. 23). In this method a new energy functional is defined by adding a Hubbard-like term to the LSDA total-energy functional:

$$E^{\mathrm{LDA}+U}=E^{\mathrm{LSDA}}+E^{U}-E^{\mathrm{dc}}, \tag{1}$$

where E^{LDA} is the LSDA energy functional, E^{U} takes into account on-site Coulomb and exchange interactions, and E^{dc} is the so-called double counting term which subtracts the averaged Coulomb and exchange interactions already in-

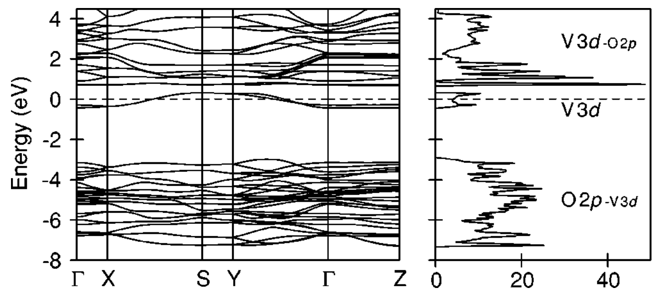

FIG. 1. LDA band structure and the total DOS calculated for α'–NaV_2O_5.

cluded into E^{U}. Neglecting nonspherical contributions to the on-site Coulomb and exchange integrals U and J the E^{U} term can be written as

$$E^{U}=\frac{1}{2}\sum_{\sigma,i,j\neq i}(U-J)n_{i\sigma}n_{j\sigma}+\frac{1}{2}\sum_{\sigma,i,j}Un_{i\sigma}n_{j-\sigma}, \tag{2}$$

where $n_{i\sigma}$ is the occupancy of the ith localized orbital with the spin projection σ. In the present work we use the E^{dc} defined as[24]

$$E^{\mathrm{dc}}=\tfrac{1}{2}UN(N-1)-\tfrac{1}{2}J\big(N^{\uparrow}(N^{\uparrow}-1)+N^{\downarrow}(N^{\downarrow}-1)\big). \tag{3}$$

Differentiating Eq. (1) over orbital occupancies gives the expression for the orbital-dependent one-electron potential:

$$V_{\sigma}^{\mathrm{LDA}+U}=V_{\sigma}^{\mathrm{LSDA}}+\sum_{i}(U-J)(\tfrac{1}{2}-n_{i\sigma})|i\sigma\rangle\langle i\sigma|, \tag{4}$$

where $|i\sigma\rangle\langle i\sigma|$ is the projector onto the localized orbital. The screened U and J which are the parameters of the model can be determined from constrained density-functional calculations.[25] Alternatively, the value of U can be obtained from photoemission data.

The electronic structure of different models for the CO phase of α'-NaV_2O_5 was calculated for the unit cell doubled along the b direction. A lattice distortion caused by charge ordering was not taken into account. To minimize possible errors the total-energy calculations for the structures with different charge and magnetic order were performed using the same mesh of 256 **k** points in the corresponding BZ and with the same maximal angular quantum numbers used for decomposition of the LMTO wave functions.

III. RESULTS AND DISCUSSION

A. LDA band structure and TB parameters

The calculated LDA band structure and total DOS of α'-NaV_2O_5 (Fig. 1) are in good agreement with the results obtained from FLAPW (Ref. 6) and pseudo potential[26] calculations. The lower part of the valence band is formed mainly by O $2p$ states with a bonding hybridization with V $3d$ states. It is separated by a gap of ≈ 3 eV from the bottom of V $3d$ states which gives a predominant contribution to the bands at and up to ≈ 4 eV above the Fermi level. It should be noted that in contrast to experimental data LDA predicts α'-NaV_2O_5 to be metallic.

Contributions from states of different symmetry (d_{xy}, d_{xz}, . . .) to the density of V d states are shown together

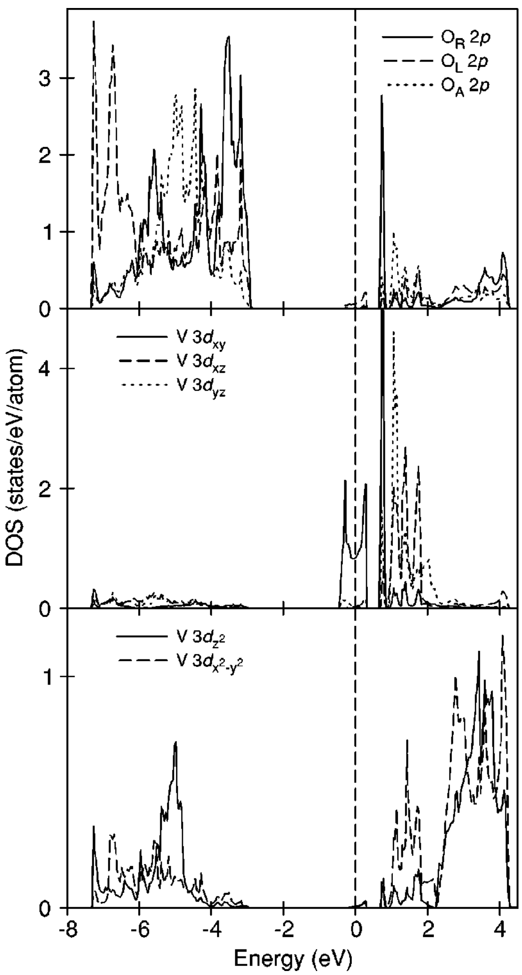

FIG. 2. DOS curves calculated for V $3d$ states of different symmetry and for $2p$ states of inequivalent oxygen sites in α'-NaV_2O_5.

with the density of O p states in Fig. 2. Compare again Fig. 3 below for the orientation of the relevant orbitals with respect to the lattice, in particular the vanadium-oxygen xy plane. The two V d bands crossing the Fermi level and the next two less than 1 eV above are formed mainly by V d_{xy} states with O_R p states giving significant contribution to the upper two. In the simplest tight-binding (TB) model which takes into account only the hybridization of V d states with p states of the nearest O atoms and neglects the distortion and tilting of the VO_5 pyramid, the V d_{xy} orbital forms $dp\pi$ bonds with the p_y orbital of the O_R atom and $p_{x,y}$ orbitals of the O_L atoms in the base of the pyramid and does not hybridize with the nearest to V apex oxygen (O_A above and below the drawing plane of Fig. 3). The states in the energy range 1–2 eV are mainly of V $d_{xz,yz}$ character. They are shifted to higher energy relative to V d_{xy} states by a small $dp\sigma$ contribution of antibonding hybridization with $p\sigma$ orbitals of the O atoms forming the base of the pyramid, which is due to a small displacement of the V ions out of the basal plane of the pyramid. Finally, the bands above ≈ 2 eV originate from V $3d_{z^2}$ and $3d_{x^2-y^2}$ states which form $dp\sigma$ antibonding states with O_A p_z and $O_{R,L}p_{x,y}$ orbitals, respectively. It is interesting to note that this picture of the chemical bonding in α'-NaV_2O_5 with the bands crossing the Fermi level formed by relatively weakly hybridized V d_{xy} states is in some sense complementary to the case of layered cuprates where the highest occupied states originate from strongly antibonding Cu $d_{x^2-y^2}$–$Op_{x,y}$ states of $dp\sigma$ character. Here, the V ion resides in the interior of a pyramid whose basal square has its diagonals in x and y directions and whose apex is on the z axis. Four of the five d orbitals of vanadium can make bonds partially of σ character with p orbitals of oxygen ions at the corners of the pyramid, except for the d_{xy} orbital, which for symmetry reasons can only make π bonds. Hence, we have π bands around the Fermi level in an ionicity gap of σ bands, and vanadates are π-electron systems. This explains the small bandwidths already on the mean-field level.

The two pairs of bands formed by V d_{xy} are of key importance for understanding the electronic properties of α'-NaV_2O_5. These bands are separated by a small gap of ≈ 0.2 eV from the higher bands with the splitting between the pairs being $\approx 0.5-1$ eV (see Fig. 1). The two bands crossing the Fermi level exhibit rather strong dispersion along the Γ-Y direction and to a lesser extent along Γ-X whereas the other two bands are almost dispersionless. All four bands show no appreciable dispersion along the Γ-Z direction.

An effective TB model constructed so as to reproduce the calculated band structure is a very useful tool which helps to understand the details of the chemical bonding and can be used as a basis for construction of more involved many-body Hamiltonians. Such a TB model for the four lowest-lying V $3d$ bands in α'-NaV_2O_5 was proposed in Ref. 6. This simple model written in terms of effective V-V hopping integrals reproduces well the dispersion of the lower pair of the bands and the average splitting between the pairs. However, it fails to account for the strongly suppressed dispersion of the upper two bands along the Γ-Y direction. Also, the model contains the hopping terms between rather distant V atoms and it is difficult to estimate in advance which of these terms should be included in the model.

Our aim is to explain the above-mentioned difference in the dispersion of the four V d_{xy} bands; therefore, we consider in the present paper an extended TB model based on explicit V-O hopping. As follows from the analysis of the density of states (DOS) (Fig. 2) and the LMTO eigenfunctions, relevant for the TB model are V d_{xy}, O_Rp_y, and $O_Lp_{x,y}$ orbitals. To distinguish between two types of O_L atoms surrounding a V site we shall use where necessary the notation O_L' for the oxygen atom lying at the continuation of the V-O_R-V rung whereas the atoms placed along the V chain running along the b direction will still be denoted as O_L. With the appropriate choice of a unit cell neither of the V d_{xy}–$O_L'p_y$ bonds crosses the cell boundary and the $O_L'p_y$ orbitals can be excluded from the model, their effect being taken into account implicitly via renormalization of the remaining hopping terms. In other words, d_{xy} in our model is the antibonding V d_{xy}–$O_L'p_y$ molecular orbital (MO) rather than the atomiclike V d_{xy} orbital.

The dispersion of the lower pair of V d_{xy} bands can be reproduced already within the TB model which includes only four hopping matrix elements [see Fig. 4(a)]. Strong V d_{xy}–O_Rp_y hybridization ($t_{VO_R}=1.7$ eV) is responsible for the splitting of the four bands into two subbands. The dispersion along the Γ-Y direction is due to V d_{xy}–O_Lp_x hop-

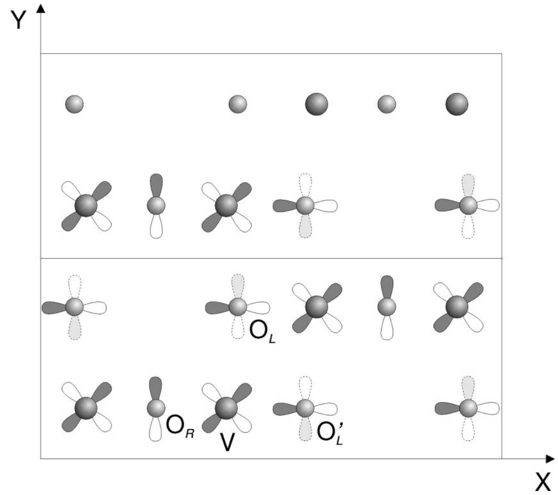

FIG. 3. Schematic representation of the orbitals used for the extended TB model. $O'_L p_y$ orbitals included implicitly via renormalization of the other hopping terms are plotted by dashed line.

ping ($t_{VO_L}=1.0$ eV) whereas the band crossing in this direction is provided by the direct σ hopping between $O_L p_x$ orbitals ($t_{O_L O_L}=0.6$ eV). Finally, the small matrix element $t_{VV}=0.032$ eV between V d_{xy} orbitals governs the dispersion along the Γ-X direction. As was mentioned above we assume in the model that d_{xy} is an antibonding V d_{xy}–$O'_L p_y$ MO and the effective t_{VV} term includes not only direct d_{xy}–d_{xy} hopping but also the hopping term of the same sign between $O_L p_y$ orbitals participating in the MO. Moreover, as

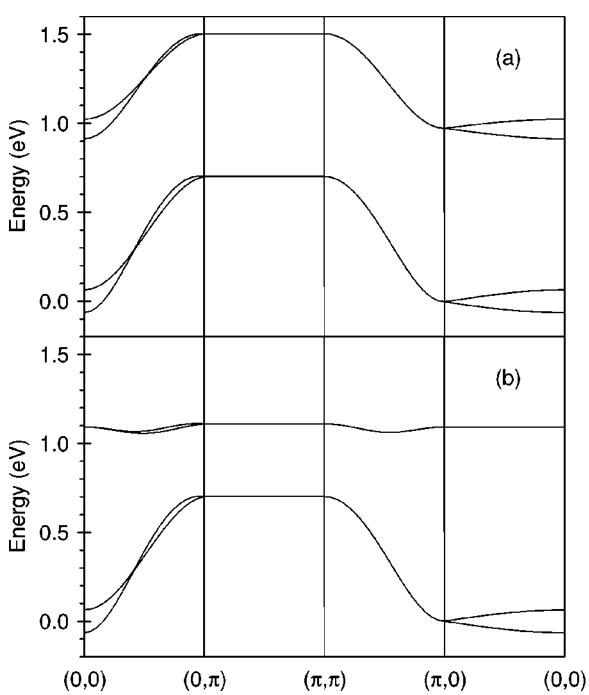

FIG. 4. (a) The dispersion of the V d_{xy} bands calculated from the extended TB model with four hopping terms $t_{VO_R}=1.7$ eV, $t_{VO_L}=1.0$ eV, $t_{O_L O_L}=0.6$ eV, and $t_{VV}=0.032$ eV (see text). (b) The same as (a) but with additional hopping terms $t_{O_R O_L}=0.8$ eV, $t_{O_R O_R}=0.4$ eV, and $t'_{VO_R}=0.025$ eV which suppress the dispersion of the upper pair of the bands.

O_L atoms are slightly shifted away from the V chains running along the b direction the hopping terms between the V d_{xy} orbital and the p_y orbital of O_L atoms from the same chain give a nonvanishing contribution to t_{VV}. The sign of this term is determined by the direction of the out-of-chain displacement of O_L atoms. For the experimentally observed displacement toward the V atom from another ladder the sign is opposite to the sign of the direct d_{xy}–d_{xy} hopping, thus decreasing the effective t_{VV}.

To verify whether the compensation of the individual contributions to t_{VV} really occurs we performed calculations with an enlarged out-of-chain displacement of O_L atoms along the a direction. As a result of the O_L shift V–O_L and O'_L–O_L distances decrease by 1.5% and 1.8%, respectively, while the V-V distances remain unchanged. If the V d_{xy}–$O_L p_y$ hybridization were weak one would expect a small increase of the splitting of the lower pair of V d_{xy} bands at the Γ point due to stronger p_y-p_y hopping. The calculated splitting decrease, however, from 0.15 eV for the original structure to 0.08 eV for the distorted one, indicating that the effective t_{VV} is very sensitive to the relative position of V and O_L atoms.

As can be seen from Fig. 4(a) the TB model with the four hopping terms gives nearly the same dispersion for both lower and upper pairs of the V d_{xy} bands, and additional hopping terms should be included to reproduce the flatness of the upper bands. We found that their strong dispersion along the Γ-Y direction can be suppressed [see Fig. 4(b)] by ‘‘switching on’’ $O_R p_y$–$O_L p_x$ ($t_{O_R O_L}=0.8$ eV) and $O_R p_y$–$O_R p_y$($t_{O_R O_R}=0.4$ eV) hybridizations, both at least in part of the σ character. As the effect of both these terms on the dispersion is similar the values of $t_{O_R O_L}$ and $t_{O_R O_R}$ were determined using their ratio estimated from the distances between the corresponding oxygen atoms and the mutual orientation of the orbitals. The remaining dispersion of the upper pair of bands along Γ-X is canceled by the hopping term $t'_{VO_R}=0.025$ eV between the V d_{xy} MO and p_y orbital of the O_R atom from another ladder.

The dispersion of the lower pair of the V d_{xy} bands is not affected by the three above-mentioned hopping terms as all of them act via $O_R p_y$ orbitals which give only a small contribution to the corresponding wave functions. The analysis of the eigenfunctions shows that at the Γ point the V d_{xy} orbitals centered at the ends of a rung have the same phases and, consequently, they are orthogonal to the $O_R p_y$ orbital. At the arbitrary k point the orthogonality is not perfect due to the weak interladder coupling along the a direction but as the corresponding hopping term t_{VV} is very small the contribution of $O_R p_y$ orbitals to the wave function remains negligible. On the contrary, the $O_R p_y$ orbitals contribute strongly to the wave functions of the upper pair of the V d_{xy} which are π antibonding with respect to V d_{xy}–$O_R p_y$ hybridization.

The conclusion can be derived that these additional hopping terms are not important when describing the low energy electronic excitations in α'-NaV_2O_5. This is true, however, only for the high-temperature phase in which all V sites are equivalent. Below T_c when V^{4+} and V^{5+} ions can occupy different ends of the same rung the $O_R p_y$ contribution to the wave functions corresponding to the lowest V d_{xy} bands can be substantial and the dispersion of these bands will be determined to a great extent by the hopping terms in which the O_Rp_y orbitals are involved.

Figure 4(b) shows that the proposed extended TB model reproduces the dispersion of all four V d_{xy} bands. The hopping terms obtained from the comparison of this model to a TB model written in terms of effective V-V interactions are close to those given in Ref. 6. An important difference is the appearance of an additional hopping term $t_d = 0.085$ eV which couples d_{xy} orbitals of V atoms placed at the opposite ends of consecutive rungs of a ladder. This term has been found to be of the same absolute value as the hopping along the leg of a ladder $t_\parallel$ but of the opposite sign and is necessary to compensate the dispersion of the upper pair of bands along the Γ-Y direction produced by the latter. As both $t_\parallel$ and t_d give the contribution of the same sign to the dispersion of the lower bands we have obtained the value of $t_\parallel = -0.085$ eV which is two times smaller compared to the value of -0.17 eV found in Ref. 6. It should be pointed out that the comparatively large t_d can be responsible for exchange coupling of V^{4+} ions along the b direction which is necessary to explain the strong dispersion of magnetic excitations along the Γ-Y direction in the case of the ordering of V^{4+} into zigzag chains which is considered as a possible low-temperature structure of α'-NaV_2O_5.

B. LDA+U results

The electronic structure of the low-temperature phase of α'-NaV_2O_5 was studied using the LDA+U approach. We restricted ourselves to the consideration of CO structures which are possible in the unit cell doubled along the b axis thus neglecting the experimentally observed increase of the unit cell along the a and c axes. The lattice distortion caused by CO was not taken into account and the atomic positions determined for the high-temperature phase[5] were used. The LDA+U calculations were performed using the value of 3 eV for $U_{\mathrm{eff}} = U - J$. The values of screened on-site Coulomb $U = 4.1$ eV and exchange $J = 1.1$ eV integrals were determined from supercell calculations.[25] The calculated U is significantly smaller than $U = 6.82$ eV used for V^{4+} ions in α'-NaV_2O_5 in Ref. 27 which can be explained by the fact that in our supercell calculations V d_{z^2} and $d_{x^2-y^2}$ orbitals which form rather strong $dp\sigma$ bonds with O p orbitals were allowed to participate in the screening of excessive V d charge thus providing more perfect screening compared to the case when all V d electrons are treated as localized.[28]

The electronic structure and total energies were calculated for two models for the CO phase which have commonly been considered as possible candidates for the low-temperature structure. In the first model [Fig. 5(a)] magnetic V^{4+} ions form in-line chains along the b direction separated by nonmagnetic chains of V^{5+} ions. The second one [Fig. 5(b)] consists of zigzag chains of V^{4+} ions occupying alternating ends of consecutive rungs of a ladder. For each of these models different kinds of magnetic ordering of V^{4+} moments were considered.

The band structure and the total DOS for the model with the in-line CO and antiferromagentic (AF) ordering of V^{4+} magnetic moments along the chains [cf. Fig. 5(a)] are shown in Fig. 6(a). The two highest occupied bands that are doubly degenerate due to AF order are formed by d_{xy} orbital combinations of the four V^{4+} ions, the d_{xy} states with opposite spin are pushed to higher energies by the on-site Coulomb repulsion U. These almost dispersionless bands are ≈2 eV above the Fermi level and are separated by an energy gap of ≈1 eV from the lowest unoccupied $V^{5+} d_{xy}$ band. In the case of ferromagnetic (F) intrachain ordering and AF ordering along the a direction [Fig. 6(b)] the hybridization between $V^{4+} d_{xy}$ orbitals along the chains via $O_L p_x$ orbitals leads to the appearance of relatively strong dispersion along

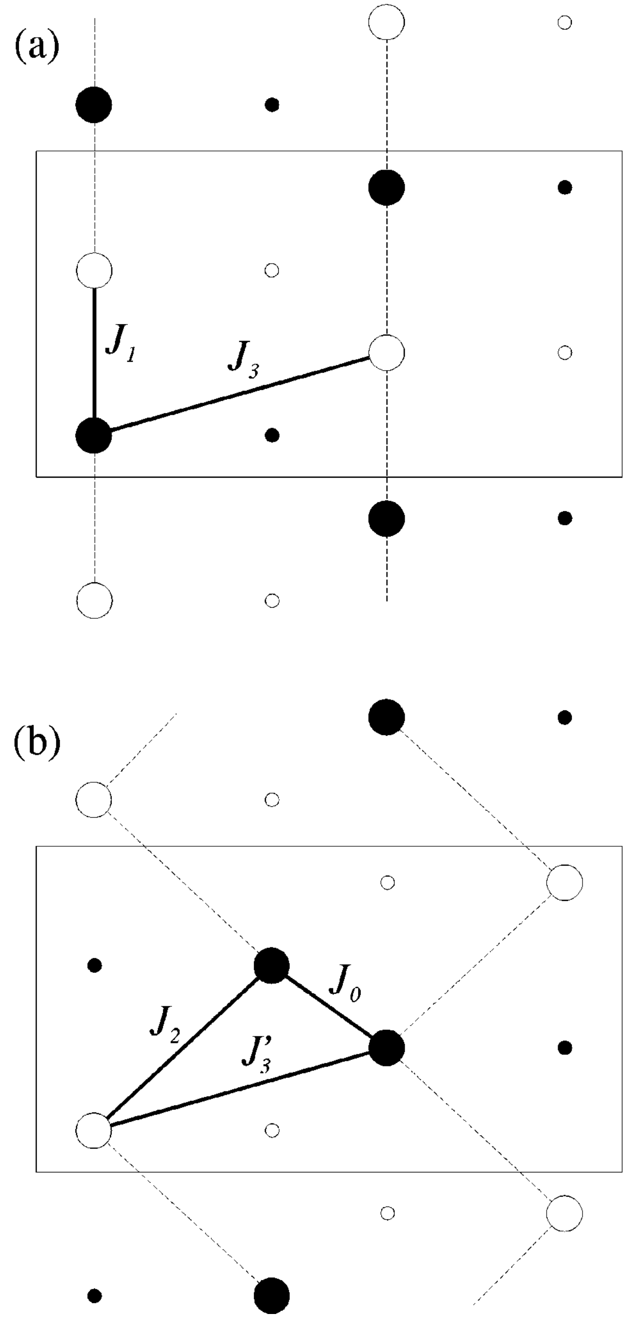

FIG. 5. (a) In-line charge ordering of V^{4+} ions. (b) Zigzag charge ordering of V^{4+} ions. Big solid circles, V^{4+} spin up; big open circles, V^{4+} spin down; small open and closed, circles V^{5+}. The nominally V^{5+} ions inherit a small spin moment from their V^{4+} partners in the same rung, see text.

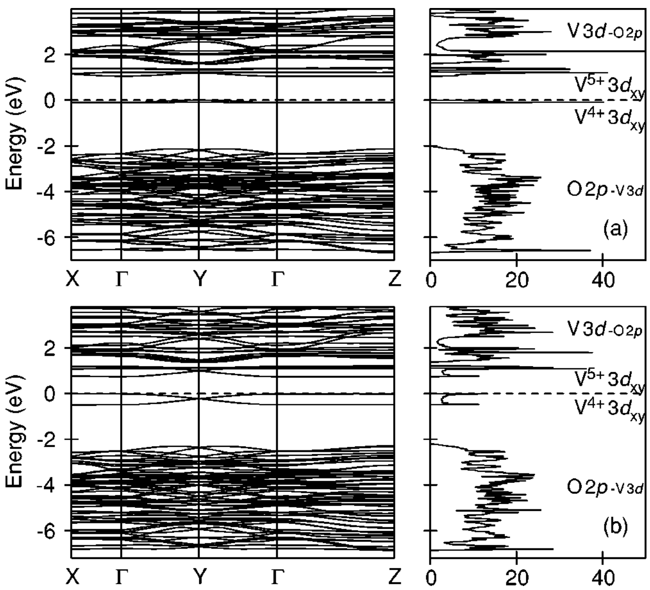

FIG. 6. LDA+U band structure and the total DOS for two different kinds of magnetic ordering of V^{4+} moments within the in-line CO model: (a) AF intrachain ordering; (b) F intrachain and AF interchain ordering.

the Γ-Y direction. As a result of the band broadening the correlation gap decreases to 0.7 eV.

The dispersion of the highest occupied V^{4+} and the lowest unoccupied $V^{5+}d_{xy}$ bands calculated for the zigzag CO model with either AF [Fig. 7(a), spin pattern of Fig. 5(b)] or F [Fig. 7(b)] ordering of V^{4+} magnetic moments along the zigzag chains is very similar to that obtained for the corresponding cases within the in-line CO model. These results illustrate the importance of the above-mentioned effective t_d hopping matrix element which couples d_{xy} orbitals of V ions occupying the opposite ends of consecutive rungs of a ladder. As in the CO phase the V ions at the ends of a rung are no longer equivalent; in contrast to the LDA calculations $O_R p_y$ orbitals contribute to the wave functions of the lowest $V^{4+}d_{xy}$ bands and the hybridization via $O_R p_y$ orbitals responsible for t_d is ''switched on'' for these bands. Note that the resulting features of the band structures shown in Fig. 7 are obtained from full LDA+U calculations independent of the tight-binding model and hence prove the correctness of our tight-binding model in this respect.

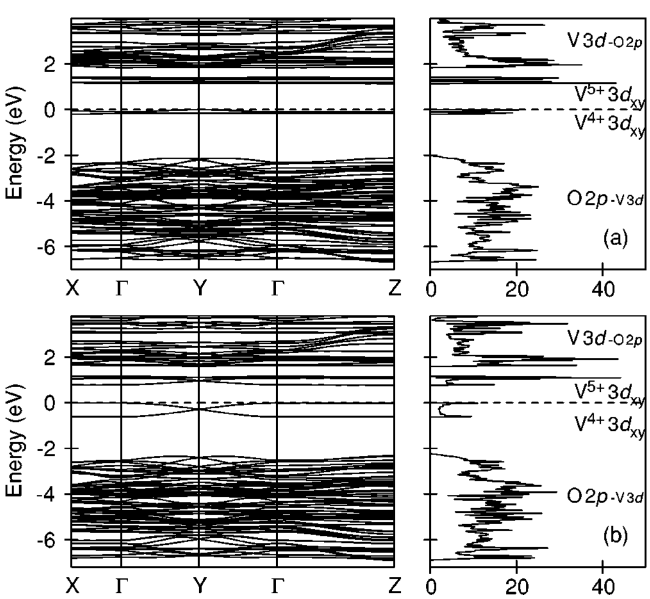

FIG. 7. LDA+U band structure and the total DOS for two different kinds of magnetic ordering of V^{4+} moments within the zigzag CO model with (a) AF intrachain and F interchain ordering; (b) F intrachain and AF interchain ordering.

TABLE I. The total energies per formula unit calculated with the LDA+U method for various models for charge and magnetic ordering in α'-NaV_2O_5. The lowest energy of the zigzag CO model with AF intrachain and F interchain magnetic ordering is taken as zero energy.

Model	Charge order	Magnetic order intra	Magnetic order inter	E(meV)
E^z_{af}	zigzag	AF	F	0.0
E^z_{aa}		AF	AF	2.0
E^z_{ff}		F	F	13.9
E^z_{fa}		F	AF	20.8
E^i_a	in line	AF		15.5
E^i_{ff}		F	F	27.5
E^i_{fa}		F	AF	32.5

Another important consequence of the strong hopping across the rung is that the $V^{4+}d_{xy}$ orbital can hybridize via $O_R p_y$ with the unoccupied d_{xy} orbital of the V^{5+} ion from the same rung and the latter gives a substantial contribution to the wave functions of the occupied $V^{4+}d_{xy}$ bands. This partial delocalization of $V^{4+}d_{xy}$ states can lead to the appearance of relatively long-range terms in a TB model describing the effective $V^{4+}d_{xy}$–$V^{4+}d_{xy}$ hopping in the case of the CO structure with one V^{4+} ion per rung. The degree of the delocalization depends on the relative energy positions of the V^{4+} and $V^{5+}d_{xy}$ states which can be rather sensitive to the changes of the V-O distances in the VO_5 pyramid caused by charge ordering. As a result of the $V^{4+}d_{xy}$–$V^{5+}d_{xy}$ hybridization the V^{4+} spin magnetic moment, defined as an integral of the electron spin density over the atomic sphere surrounding the ion, is smaller than the value of 1 μ_B expected for spin $\frac{1}{2}$ and is equal to ≈0.9 μ_B for both zigzag and in-line CO models. However, together with the moment of about 0.1 μ_B inside the V^{5+} sphere this gives the total magnetic moment of 1 μ_B per rung. Just as for the TB model this smearing of the V^{4+} magnetic moment over the rung can affect the parameters of the effective model for exchange interactions between V^{4+} spins in the CO phase of α'-NaV_2O_5.

The total energies obtained from the LDA+U calculations for the CO models with different kinds of magnetic order are summarized in Table I. The lowest total energy is calculated for the zigzag CO model with AF alignment of V^{4+} moments along the chains and F inter-chain ordering [E^z_{af}, Fig. 5(b)]; the energy of the same model but with AF interchain ordering (E^z_{aa}) being only 2 meV higher. The difference between the lowest energies of the considered CO models is found to be 15.5 meV. Comparison of the total energies of the models with different types of magnetic order indicates clearly that AF intrachain magnetic order is preferable for both in-line and zigzag CO models. Calculations were also performed for some other models for CO possible in the $1\times2\times1$ supercell but their total energies were found to be much higher than those of the zigzag and in-line models. For example, an interchange of V^{4+} and V^{5+} at every second ladder in the in-line CO model leads to double chains along the *b* direction. This increases the total energy by 125 meV. Another possible type of CO is a structure with one or two rungs doubly occupied by V^{4+} ions. We have found, however, that the formation of the doubly occupied rung results in the energy loss of about 100 meV.

The conclusion derived from the LDA+U calculations that the zigzag CO model [Fig. 5(b)] is more favorable than the in-line one is supported by recent experimental data on the temperature dependence of the dielectric constant in α'-NaV_2O_5.[29,30] The observation of steplike anomalies at T_c suggests that the low-temperature structure is of the antiferroelectric type which is consistent with the zigzag CO model. The in-line CO model, on the other hand, corresponds to the ferroelectric ordering with the spontaneous electric polarization along the *a* axis in which case a peak in the temperature dependence of the dielectric function should be observed.

C. Effective exchange constants

Effective exchange constants between V^{4+} spins are necessary input values for theoretical models aimed at the description of magnetic excitations in α'-NaV_2O_5. In the present work they were estimated by mapping the LDA+U total energies onto the mean-field energy of a localized Heisenberg model. Assuming that the total-energy differences between the configurations with the same CO but different orientations of V^{4+} magnetic moments are due to the change of the magnetic energy written as a sum of pair interactions of the Heisenberg form one can express the exchange constants in terms of the total-energy differences. The corresponding expressions for the exchange parameters introduced for the zigzag (J_0, J_2) and in-line (J_1) CO models (Fig. 5) are

$$J_0=-2[(E^z_{aa}-E^z_{af})+(E^z_{fa}-E^z_{ff})],$$

$$J_1=(E^i_{ff}-E^i_{a})+(E^i_{fa}-E^i_{a}),$$

$$J_2=(E^z_{fa}-E^z_{af})+(E^z_{ff}-E^z_{aa}),$$

where all the energies are given per formula unit, the upper index specifies the CO model whereas the first and the second letter in the subscript denotes the kind of the intrachain and interchain magnetic ordering, respectively. Here we assume additionally that the absolute value of V^{4+} spin is equal to $\frac{1}{2}$ and remains constant. Similar expressions can be written for J_3 and J_3' exchange parameters.

The effective exchange coupling parameters calculated from the LDA+U total energies are given in Table II. We found that the most important parameters are $J_1=29.0$ meV and $J_2=32.7$ meV responsible for the exchange coupling along the in-line and zigzag chains, respectively. While the exchange coupling along the in-line chains is provided by the superexchange via $O_L 2p_x$ orbitals the mechanism for J_2 is less obvious. It can be explained by the effective hopping of $V^{4+}3d_{xy}$ orbitals via O_R2p_y–O_L2p_x and O_R2p_y–O_R2p_y paths taking into account the large values of the corresponding hopping terms $t_{O_RO_L}$ and $t_{O_RO_R}$ (see Sec. III A) obtained from the TB fit to the LDA results. The important point here is that in contrast to the LDA results, in the case of the CO phase with inequivalent V ions at the ends of a rung, the O_R2p_y orbital contributes to the wave functions of occupied $V^{4+}d_{xy}$ bands. An additional contribution to J_2 can appear as a result of the above-mentioned partial delocalization of the $V^{4+}d_{xy}$ orbital over the rung due to its hybridization with the d_{xy} orbital of the V^{5+} ion. Then, these delocalized orbitals of adjacent rungs can hybridize via O_Lp_x orbitals which gives an additional channel for the interaction between V^{4+} spins.

TABLE II. The effective exchange-coupling constants calculated from the LDA+U total energies for the in-line and zigzag CO models.

	CO	J(meV)
J_1	in line	29.0
J_3		−5.0
J_0	zigzag	−18.0
J_2		32.7
J_3'		−4.9

The calculated exchange constants are smaller than the value of 560 K (48.3 meV) estimated from the high-temperature magnetic susceptibility using the formulas for the spin-$\frac{1}{2}$ chain.[2] However, the present calculations were performed for the case of nearly complete charge ordering and it is difficult to compare the results to those obtained for the high-temperature phase with the average oxidation state of V ions being $V^{4.5+}$. Another possible reason for the discrepancy is that the on-site Coulomb repulsion U derived from the supercell calculations may be overestimated leading to underestimated values of the exchange parameters. Indeed, J_1 and J_2 calculated with $U_{\mathrm{eff}}=2$ eV are about 60 meV which is already larger than the experimental value.

An important consequence of the fact that the intrachain exchange coupling for both CO models is of comparable strength is that the experimentally observed strong dispersion of magnetic excitations in the Γ-Y direction can be explained not only in the case of the in-line CO model but also within the CO model with the zigzag ordering of V^{4+} ions. A detailed study of the magnetic excitations in α'-NaV_2O_5 using the calculated exchange parameters has been given in Ref. 16.

The interchain coupling is determined by ferromagnetic effective exchange constants $J_3=-5.0$ meV for the in-line CO model and $J_0=-18.0$ meV and $J_3'=-4.9$ meV for the zigzag one. This surprisingly large value of J_0 questions the applicability of the model of weakly coupled AF V^{4+} zigzag chains. However, at least for small deviations from the ground state with AF intrachain ordering the energy gain from ferromagnetic alignment of the V^{4+} moments coupled by J_0 is almost exactly compensated by the energy loss due to antiparallel alignment of the moments coupled by J_3'. As a result of this compensation the total energies E^z_{af} and E^z_{aa}

of two configurations with different alignment of the nearest V^{4+} moments differ by 2 meV only.

The effective hopping between d_{xy} orbitals of the nearest V ions is much smaller than the hopping along the ladders and it can hardly account for the large ferromagnetic J_0. The dominant mechanism responsible for this interaction is the almost 90° exchange caused by the hybridization of the $V^{4+}d_{xy}$ orbital via $O_L p_{x,y}$ states to unoccupied $d_{xz,yz}$ and $d_{x^2-y^2}$ orbitals with the same spin projection of the V^{4+} ion from the adjacent ladder. As the latter states are split by ≈ 1 eV by the on-site exchange coupling the energy gain from this hopping depends on the relative orientation of the V^{4+} magnetic moments and reaches its maximal value when the moments are ferromagnetically aligned. To verify that this mechanism is the most important one we have determined J_0 from test calculations with the on-site exchange interaction switched off which was achieved by averaging the LSDA exchange-correlation potential for the majority and minority spin electrons. J_0 calculated in this way was found to be ten times smaller in absolute value and of opposite sign which confirms that it is really governed by the on-site exchange. On the other hand, calculated in the same manner J_2 does not change so drastically as it is determined mainly by the on-site Coulomb repulsion U.

As the V^{4+} ions coupled by J_3 and J_3' occupy equivalent crystallographic positions one can suppose that the values of these exchange parameters should be close to each other and their difference can be used to check the numerical accuracy of the total-energy calculations. Indeed, the calculated values of J_3 and J_3' differ only slightly which confirms that the calculations were performed with sufficient accuracy.

To our opinion this relatively strong exchange coupling, considering the large distance between the corresponding V^{4+} ions, is caused by the partial redistribution of a V^{4+} spin between d_{xy} orbitals of V^{4+} and V^{5+} ions from the same rung. The mechanism responsible for J_3 and J_3' is similar to that for J_0 with the important difference that for the former the hybridization path between d_{xy} and unoccupied $d_{xz,yz}$ orbitals is longer and includes additionally $O_R p_y$ and $V^{5+}d_{xy}$ states which leads to a significant decrease of J_3' compared to J_0.

IV. SUMMARY AND CONCLUSIONS

The extended TB model based on explicit V-O hopping which describes the dispersion of the four bands formed by V d_{xy} states has been constructed by fitting the parameters to the band structure of α'-NaV_2O_5 calculated using the LMTO method. Taking into account the hopping terms between oxygen p orbitals allows us to reproduce the suppressed dispersion of the upper pair of V d_{xy} derived bands. The Op–Op hybridization is especially important in the case of the CO phases as it affects the dispersion of the occupied $V^{4+}d_{xy}$ bands and leads to an important additional hopping term in an effective vanadium-only tight-binding model, which has not been considered previously.

From the results of LDA+U calculations performed for different models for the CO phase of α'-NaV_2O_5 it has been found that the energy of the CO model with zigzag ordering of V^{4+} ions is lower than the energy of the in-line CO model. Relatively strong dispersion of V^{4+} d_{xy} bands is observed for both CO models when V^{4+} moments are ordered ferromagnetically along the corresponding chains.

Effective exchange constants between V^{4+} magnetic moments were determined from the comparison of the LDA +U total energies calculated for different kinds of MO within the zigzag and in-line CO models. It was found that for both CO models the strongest exchange interaction is the AF intrachain coupling, whereas the coupling between the moments of the nearest V^{4+} ions in the case of the zigzag CO model was found to be ferromagnetic. The calculated exchange constants are compatible with the experimental values determined from the high-temperature susceptibility. The calculated intrachain exchange coupling for both in-line and zigzag CO models is of comparable strength. The important consequence is that the experimentally observed strong dispersion of magnetic excitations in the Γ-Y direction can be explained not only in the case of the in-line CO but also within the CO model with the zigzag ordering of V^{4+} ions.

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