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A comparative study of Coulomb-correlated electronic structure of the one dimensional spin-Peierls compound α'-NaV_2O_5 in $Pmmn$ and $P2_1mn$ crystal structure

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A comparative study of Coulomb-correlated electronic structure of the one dimensional spin-Peierls compound α '-NaV_2O_5 in *Pmmn* and $P2_1mn$ crystal structure

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Abstract

The paramagnetic, spin-polarized, and LDA+U rotationally invariant, fully self-consistent linear-muffin-tin orbital band structure for the second inorganic spin-Peierls vanadate α '-NaV_2O_5 has been calculated for both centrosymmetric *Pmmn* and noncentrosymmetric crystal structure and two supposed antiferromagnetic orderings. A very small band gap solution and magnetic moments on vanadium atoms are obtained in the framework of local-spin-density functional approximation (LSDA). The new rotationally invariant LDA+U approach has produced the insulating antiferromagnetic solution with more appropriate energy gaps and magnetic moments. We found that the minimal crystal structure changes produce significant changes in the electronic structure and magnetic properties. Starting from an extended four-band tight-binding model, fitted to the paramagnetic *Pmmn* bands, the hopping terms relevant for the calculation of exchange parameters of a spatially anisotropic Heisenberg model are estimated. A new frustrating second neighbour coupling, as well as a pronounced diagonal intraladder hopping term, are found.

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I. INTRODUCTION

The rich variety of electrical conduction exhibited by the transition-metal oxides has made them a lively area of research for the last several decades [1,2]. We are witnessing a renewed interest in physical properties of these oxides of various types. That interest has grown after the discovery of high-T_C superconductors and joined efforts of many workers to understand the origin of high-temperature superconductivity in various copper-oxide ceramics [3–5].

Besides high-T_C superconductors, an exceptional variety of new materials have been discovered that cannot be understood at all with traditional ideas. These are, for instance, cuprate $CuGeO_3$-the first inorganic compound containing spin-1/2 CuO_2 chains along the orthorhombic *c*-axis, exhibiting a spin-Peierls (SP) transition [6,7], newly discovered one-dimensional (1D) strontium-copper-oxide chain and ladder compounds [8–11], perovskite oxides $La_{1-x}Ca_xMnO_3$ with colossal magnetoresistance in the La-Ca-Mn-O and related films [12–14] etc.

One of the remarkable ground states we faced in the quasi one-dimensional systems is the SP ground state. At low temperatures (below the transition temperature T_{SP}) a magnetoelastic coupling occurring in a system of one-dimensional spin-1/2 chains coupled with the three-dimensional phonons leads to the dimerization of the magnetic lattice, the formation of a gap in the spectrum of magnons, and exponential temperature decrease of the magnetic susceptibility. The opening of a magnetic gap is usually accompanied by a structural transition. The discovery of a SP state in an inorganic compound $CuGeO_3$ [6] has revived strong interest in this phenomenon, due to the fact that it enabled detailed studies of a SP-system on large single crystals for the first time, as well as the investigations of the influence of impurities on the properties of a SP ground state. The problem of the spin-Peierls transition is of a general importance for solid state physics. It is well known that 1D linear chain with a magnetic interaction cannot exhibit long-range order at non-zero temperatures, so that the element of 'chaos' is favourable even approaching zero temperature.

The common denominator of all these systems is the dominant role played by electron-electron interaction effects in governing the physical properties of them. Such systems are collected together under the general heading 'highly correlated electron systems'.

"These materials are typically characterized by the existence of different kinds of order, including charge and orbital and spin density waves, together with superconducting and magnetic order. Indeed, these different kinds of ordering, which are conventionally thought to compete with each other, instead often appear to be synergistic in these materials. Such systems may also exhibit quantum fluid ground states and exotic transitions from ordered to quantum disordered states at absolute zero temperature. The possibilities for technological applications of some of these compounds are tantalizing, but they also present some of the deepest intellectual challenges in physics" [15].

Isobe and Ueda [16] were the first workers who found a significant decrease of the susceptibility in a quasi-one-dimensional compound α'-NaV_2O_5 bellow $T_{SP} \simeq 34$ K, and they established the opening of a spin gap in this compound. They suggested that α'-NaV_2O_5 crystallizes in the orthorhombic noncentrosymmetric crystal structure described by the space group $C^7_{2v} - P2_1mn$ [17]. Several experimental measurements aimed at explaining the isotropic exponential disappearance of the spin-susceptibility, a simultaneous crystallographic distortion and the field dependence of the transition temperature – the hallmarks of the SP transition. The presence of the SP transition was originally suggested by the susceptibility measurements on polycrystalline samples [16,18,19]. Based on the dependence on magnetic field orientation, magnetic susceptibility measurements on single crystals clearly confirmed that the nature of the low-temperature phase is a spin symmetric singlet ground state [20].

Structural distortions observed by means of x-ray diffraction [21], NMR [18], Raman and infrared scattering [20,22] further suggested that an underlying spin-phonon coupling is responsible for the SP transition. The critical temperature $T_{SP} \simeq 34$ K is the highest of all known organic or inorganic SP compounds.

First theoretical investigations of the spin-Peierls α'-NaV_2O_5 were performed by using a one dimensional dimerized Heisenberg model [23], and the dimerization parameter δ was determined requiring that the model reproduces the experimentally observed spin gap Δ. A new view to the electronic structure of vanadate α'-NaV_2O_5 in centrosymmetric $D^{13}_{2h} - Pmmn$ crystal structure was suggested by Horsch and Mack [24]. They proposed an explanation for the insulating state, which is not based on a charge modulation. Using the Hubbard-type model Hamiltonian they argued that strong correlations together with the Heitler-London character of the relevant intermediate states naturally lead to antiferromagnetic Heisenberg chains.

After these first attempts, many other workers started investigations of the physics of NaV_2O_5 both experimentally and theoretically [25–29]. An important prerequisite for understanding the nature of optical, electrical, magnetic and other properties of vanadate α'-NaV_2O_5 is a detailed knowledge of its electronic structure. Several *ab initio* calculations of electronic structure both by means of standard density functional methods in the local-density-approximation (LDA), local-spin-density-approximation (LSDA) and by use of a more sophisticated LDA+U method [30] were done [31–33]. Spin-polarized calculations were done with use two different computational methods and for two different crystal structures of NaV_2O_5 [32,33].

In spite of three years of intensive studies of NaV_2O_5, an agreement with respect to the quantitative description of opposing or complementary interactions such as inter-chain coupling, frustration, spin-phonon coupling, charge ordering (CO) has not been reached, despite the qualitative understanding of their influence in different magnetically ordered states. The situation in this vanadate is evidently more complicated and interesting than in conventional SP systems. Indications that the physics of NaV_2O_5 may be different from that of, e. g., $CuGeO_3$ come from structural, magnetic, and thermodynamic data (for more details we refer the reader to the recent work of Mostovoy and Khomskii [29]).

The magnetic properties depend very sensitively on the electronic structure and electronic interactions in different measured structures. Namely, the original crystal structure was questioned [31,34,35]. According to a detailed x-ray diffraction studies at low temperatures the structure of NaV_2O_5 was identified as centrosymmetric $Pmmn$, contrary to earlier assignment $P2_1mn$ [17].

A comparative study of electronic structure of NaV_2O_5, for several possible magnetic orderings in the upper mentioned crystal structures and in the framework of a same band structure computational method, is welcomed presently. In order to fulfill this task the self-consistent spin-restricted and spin-polarized calculations will be performed both in the standard LSDA and in one of the recent successful methodological developments for strongly correlated electron systems, e.g. the LDA plus the Hubbard-type Coulomb interaction. This method is known as the LDA+U method [30]. We hope that this comparative and more complete study of electronic structure could help us in understanding interactions responsible for different possible magnetic and charge orderings in NaV_2O_5.

The layout of this paper is as follows. Firstly, in Sec. II, we describe the calculation details specific for α '-NaV_2O_5 compound. In this section we also briefly describe main characteristics of rotationally invariant LDA+U approach (we shall henceforth refer to this method only as the LDA+U method). In Sec. III we present fully self-consistent paramagnetic (LDA) and antiferromagnetic (LSDA) results for the $Pmmn$ and $P2_1mn$ orthorhombic unit cell, as well as the results of LDA+U calculations, and discuss some important improvements in the standard LSDA approach. In section IV we present simple tight-binding model for LDA bands around the Fermi level, while section V presents brief conclusion.

II. CALCULATION DETAILS

Following the approach used in our earlier work for the calculation of the electronic structure of noncentrosymmetric $P2_1mn$ α '-NaV_2O_5 [32], we will carefully consider here the same vanadate compound in centrosymmetric $Pmmn$ crystal structure which was also observed experimentally [31]. Due to the complexity of its crystal structure, the tight-binding (TB) linear-muffin-orbital (LMTO) method in the atomic sphere approximation (ASA) [36] is very suitable for the electronic structure calculations of complex compounds like this one. The accuracy of this method is quite acceptable, basis functions are very convenient for an analysis of calculated results and futher calculation using the outcome of the LMTO calculation.

It should be said, that quite recently the crystal structure redetermination for the

NaV_2O_5 by a single crystal x-ray diffraction at room temperature has appeared, indicating that this compound is in fact centrosymmetric ($D_{2h}^{13} - Pmmn$) with only one distinct V position and three inequivalent oxygen atoms [31]. (The crystal structure for $T < T_{SP}$ still remains to be determined precisely.)

In order to study $Pmmn$ α '-NaV_2O_5 thoroughly, several self-consistent LMTO-ASA band structure calculations were done. The electronic bands have been calculated using the spin-restricted and spin-polarized version of TB-LMTO-ASA method for both nonmagnetic and two supposed antiferromagnetic (AF) states. The influence of interactions beyond LDA and LSDA for α '-NaV_2O_5 was also studied. Such an approach is needed in order to enable more appropriate description of this vanadate system in which the electronic correlation effects are very important. This part of our calculations was carried out on the basis of the LDA+U method [30].

The crystal structure of α '-NaV_2O_5 consists of double chains of edge sharing distorted tetragonal VO_5 pyramids along the orthorhombic b axis. These pyramids are linked together via common corners thus forming sheets of the pyramids stacked upon each other along c axis with Na atoms located between these sheets (Fig. 1).

Carpy and Galy were the first who reported that vanadate α '-NaV_2O_5 crystallizes in an orthorhombic cell with the space group $P2_1mn$ and two formula units in the primitive cell [17]. It contains $V^{4+}(S=1/2)$-chains along the b-axis in which, above 34 K, the magnetic susceptibility of α '-NaV_2O_5 is approximately described by the AF Heisenberg linear chain with the nearest neighbour exchange coupling $J = 560$ K [16]. These chains are separated from each other by nonmagnetic V^{5+}-chains, which is the main reason for magnetic quasi-one-dimensional behaviour of this vanadate compound.

The mentioned crystal structure redetermination for the NaV_2O_5 have indicated that this compound is in fact centrosymmetric. (It is also isostructural to CaV_2O_5 and its crystal structure, for $T < T_{SP}$, still remains to be determined precisely.) The topology of the structure is practically unchanged as compared to the previous results [17]. But, these small structural changes could produce significant changes in charge ordering patterns and electronic properties. We hope that our electronic structure calculations and comparative study of two structurally similar crystalline forms of NaV_2O_5 will help us to shed more light on the observed physical phenomena in this intensively investigated quarter-filled quasi one dimensional compound.

In our study of stable solutions for band energies for the new crystal structure LDA and LSDA TB-LMTO-ASA band structure calculations were performed first. The structural parameters for orthorhombic $Pmmn$ α '-NaV_2O_5 were taken from Ref. [31] with the corresponding lattice parameters a=11.318Å, b=3.611Å, and c=4.797Å.

For the LMTO-ASA method a number of empty spheres has to be included, since they are necessary for filling a lot of empty space in the orthorhombic $Pmmn$ structure of α '-NaV_2O_5. The atomic positions used in our calculations for centrosymmetric $Pmmn$ crystal structure, are the same as in Table 1 of Ref. [31].(All details for nocentrosymmetric $P2_1mn$ crystal structure with atomic positions, empty spheres, types, and sphere sizes for the LMTO calculation are given in Ref. [32]).

As the basis functions within the atomic spheres Na (3spd), V (4sp, 3d), and O (2sp, 3d) were used. In order to allow for antiferromagnetic ordering in the vanadate α '-NaV_2O_5 we constructed $1 \times 2 \times 1$ supercell (doubling along b-axis). We consider two different magnetic orderings, which are depicted in Fig. 2. One of them (AF-1 in Fig. 2) is the same as in our earlier work for $P2_1mn$ crystal structure [32]. Bearing in mind that experimental angular-resolved photoemission measurement [37] suggests that the doubled periodicity in the b axis exists even for $T > T_{SP}$ two supposed magnetic structures are antiferromagnetic along b axis and ferromagnetic (AF-1) or antiferromagnetic (AF-2) along a axis. People usually believe that the difference of the electronic structure for ferro- or antiferromagnetic order along the a axis is small, due to an expected weak interchain interaction along a axis [33]. We are awared of the limitations of our present calculations, especially if we take into account recent findings of J. L. de Boer et al. [35] which indicate doubling of the α '-NaV$_2$O$_5$ unit cell both along the a and the b axes, and quadrupling of the c axis, implying a sixteenfold increase of the unit cell volume. All calculations were scalar relativistic, retaining all relativistic effects except spin-orbit. Exchange correlation potential of von Barth and Hedin [38] was employed.

The method of Anisimov, Aryasetiawan, Liechtenstein, and Zaanen [30] was also used in our calculations. It cured, at least partly, the deficiencies of the LDA and LSDA band structure methods in treating the Mott-Hubbard or charge transfer (CT) insulators. They helped identify the main problem of the LSDA in handling these systems. In a homogenous electron gas, the spin dependence physically originates from the Hund's rule exchange characterized by the Stoner-type exchange parameter J, while in the Mott-Hubbard and CT insulators the Hubbard U is responsible, and U is an order of the magnitude larger than J.

The basis set dependence of the original LDA+U functional [39] is thought to be introduced on artificial grounds, presently. To cure that dependence it is necessary to find regions in space where atomic characteristics have largely survived. For d or f electrons, within atomic spheres, one can expand wave functions in a localized orthonormal basis $|inlm\sigma\rangle$ (i denotes the site, n, l, m are the main, orbital and magnetic quantum numbers, and σ is the spin index). Restricting our interest to the usual situation where only a particular nl shell is partly filled, we define the d-orbital occupation matrix for correlated electrons in this shell,

$$n^{\sigma}_{mm'} = -\frac{1}{\pi}\int^{E_F} dE\ \mathrm{Im}G^{\sigma'}_{ilm,ilm'}(E), \tag{1}$$

where $G_{ilm,ilm'}(E) = \langle ilm\sigma|(E-\hat{H})^{-1}|ilm'\sigma\rangle$ are the elements of the Green function matrix in this localized representation, and $\hat{H}$ is the effective single electron Hamiltonian. In terms of the elements of this occupation matrix $\{n^{\sigma}\}$, the LDA+U functional is defined as follows [30]:

$$E^{\mathrm{LDA+U}}[\rho^{\sigma}(\vec{r}), \{n^{\sigma}\}] = E^{\mathrm{LSDA}}[\rho^{\sigma}(\vec{r})] + E^{\mathrm{U}}[\{n^{\sigma}\}] - E_{\mathrm{dc}}[\{n^{\sigma}\}], \tag{2}$$

where $\rho^{\sigma}(\vec{r})$ is the charge density for spin-σ electrons and $E^{\mathrm{LSDA}}[\rho^{\sigma}(\vec{r})]$ is the standard LSDA functional. Equation (2) asserts that LSDA suffices in the absence of orbital polarizations, while $E^{\mathrm{U}}[\{n^{\sigma}\}]$ is the Hartree-Fock type electron-electron interaction energy given by:

$$\begin{aligned} E^{\mathrm{U}}[\{n^{\sigma}\}] = \frac{1}{2}\sum_{\{m\},\sigma} & \{\langle m, m''|V_{ee}|m'm'''\rangle n^{\sigma}_{mm'} n^{-\sigma}_{m''m'''} \\ & - (\langle m, m''|V_{ee}|m'm'''\rangle - \langle m, m''|V_{ee}|m'''m'\rangle)\, n^{\sigma}_{mm'} n^{\sigma}_{m''m'''}\} \end{aligned} \tag{3}$$

where V_{ee} is the screened Coulomb interaction among the nl electrons. The last term in Eq. (2) corrects for double counting and is given by:

$$E_{\mathrm{dc}}[\{n^{\sigma}\}] = \frac{1}{2}Un(n-1) - \frac{1}{2}J[n^{\uparrow}(n^{\uparrow}-1) + n^{\downarrow}(n^{\downarrow}-1)], \tag{4}$$

where $n^{\sigma} = \mathrm{Tr}\,(n^{\sigma}_{mm})$ and $n = n^{\uparrow} + n^{\downarrow}$. U and J are screened Coulomb and exchange parameters, respectively (For more details see Ref. [30]).

In addition to the usual LSDA potential, the variation of functional (2) gives an effective single-particle potential to be used in the single-particle Hamiltonian. The matrix elements of the screened Coulomb interaction V_{ee} together with the detailed expressions for the effective single-particle Hamiltonian are given in Refs. [30]. These are expressed through the spherical harmonics and Slater integrals F^k, and we will not repeat them here.

Instead of using the LSDA supercell procedure for determining U and J parameters for α '-NaV$_2$O$_5$ we used the values U=6.82 eV and J=0.93 eV obtained in Ref. [40]. Due to the well known and significant uncertainty in determining theoretical values of the Coulomb parameter U [41], and bearing in mind that we do not have presently an experimental U value, for α '-NaV$_2$O$_5$, the upper mentioned value is quite satisfactory for the present LDA+U calculations.

The LDA+U approximation was realized in the framework of the LMTO method in the ASA approximation. All calculations were performed in the orthogonal representation of the LMTO-ASA method [36], for experimentally observed crystalline and for the supposed magnetic structures. The exchange correlation potential was again used in von Barth-Hedin form [38]. For the tetrahedron integration in the spin-restricted and spin-unrestricted calculations we used a mesh with 28 $\vec{k}$-points in the irreducible wedge of the corresponding Brillouin zone.

III. RESULTS OF THE CALCULATION

A. Paramagnetic calculations

First of all the self-consistent spin-restricted electronic band structure of orthorhombic *Pmmn* vanadate α '-NaV$_2$O$_5$ with sixteen atoms and fourteen empty spheres per unit cell was calculated using the tight-binding LMTO-ASA method [36]. The results for paramagnetic energy bands are plotted in Figure 3. This figure shows the most important vanadium energy bands for both centrosymmetric (*Pmmn*) and noncentrosymmetric ($P2_1mn$) crystal structure. We have presented these results in order to emphasize the high similarity of the bands around the Fermi level for this metallic solution with the respective bands in the first inorganic SP material cuprate CuGeO$_3$ [42]. While NaV$_2$O$_5$ in $P2_1mn$ structure has two nearly degenerate and half-filled narrow ($\sim$ 0.65 eV) conduction bands very similar to the respective bands of CuGeO$_3$, the dispersion in Γ-Y direction in centrosymmetric *Pmmn* structure is more pronounced ($\sim$ 0.9 eV), as well as the increased splitting of two parallel bands in Γ-Z direction. These bands are again fairly separated from the occupied valence manifold $\sim$ 2.5eV (not shown Fig. 3). The same feature is characteristic for the spin-restricted bands of another inorganic SP compound CuGeO$_3$. The amplitude of this split-off in energy from the occupied manifold for the vanadate α '-NaV$_2$O$_5$ is even more pronounced than in cuprate CuGeO$_3$. We can also see in Fig. 3 that the dispersion in the b axis direction (Γ-Y) is strong while the dispersion in the direction of the other orthorhombic axes is quite weak. Let us note that our spin-restricted bands near the Fermi level come mainly from V-d_{xy} orbitals of V atoms and that they are almost the same as the ones in Ref. [33].

B. LSDA TB-LMTO AF calculations

The spin-restricted band structure calculations produced metallic solution for both centrosymmetric (*Pmmn*) and noncentrosymmetric ($P2_1mn$) structure of α '-NaV$_2$O$_5$. The band structures shown in Fig. 3 indicate the instability of the nesting with twofold periodicity along b axis. One can expect an energy gap opening for such superstructure, that is for AF order along b axis. Angular resolved photoemission (ARPES) measurements suggest that the doubled periodicity exists along the b axis direction even for $T > T_{SP}$ [37], although x-ray experiments have not recorded such a doubling [33]. According to these facts we presumed that there is an AF superexchange interaction in vanadium chains along b-direction, while, due to their structural characteristics, we have chosen both ferromagnetic (F) and AF exchange coupling between the vanadium atoms in a axis direction. Three-dimensional magnetic effects are always present to some extent if non-magnetic ions separate the vanadium chains [21]. The inelastic neutron scattering spectra of Fuji *et al* [21] indicate that one can assign some higher dimensional, i.e. 2- or 3-D, reciprocal loci associated to the momentum transfer $\vec{Q}$-values. From these results one would assume a strong AF dispersion along b^* due to the expected quasi 1D interaction along b axis, and a moderate interchain coupling perpendicular to the chains. They also concluded that "it is safe to state that the magnetic correlation below T_{SP} is not as purely one dimensional as in a good 1D-Haldane system with finite gap as e.g. in Y_2BaNiO_5". In order to allow for possible AF ordering along VO_5 chains, orthorhombic cell doubled along b axis was used. We did our spin unrestricted calculations for the two magnetic orderings depicted in Fig. 2. (From now on, we shall refer to these orderings as AF-1 and AF-2.) Evidently, in both cases we suggest AF ordering along VO_5 chains in b direction so that new orthorhombic cell is doubled along this direction. Once we assumed AF order along b and a axis (AF-2). The other selection, with AF order in the b axis and the ferromagnetic order in the a axis direction (AF-1), was already used by ourselves for the investigation of $P2_1mn$ structure [32] of NaV_2O_5 . Some workers believed that the difference in the electronic structure for these two possibilities of magnetic ordering should be small due to the expected weak interaction along the a axis [33]. We have contested this statement in our present work.

Using this $1 \times 2 \times 1$ supercell we performed the standard LSDA calculations for both centrosymmetric and nocentrosymmetric structure of $\alpha\,'$-NaV_2O_5 and AF-1 and AF-2 magnetic orderings. LSDA electronic bands along several Brillouin zone (BZ) directions and total density of states (DOS) for $Pmmn$ crystal structure and both AF-1 and AF-2 orderings are given in Fig. 4. For the AF-1 magnetic order the system relaxed to the AF insulating solution with the same magnetic moments at equivalent vanadium sites (rungs of the ladders) equal to $\mu_V = 0.23\mu_B$. Very small band-gap solution of 0.12 eV and equally small magnetic moments on vanadium sites could be assumed as a manifestation of the well-known failure of the LSDA to account properly for electronic correlations in $\alpha\,'$-NaV_2O_5. The situation is even worse for $Pmmn$ structure and the supposed AF-2 magnetic structure. Gapless solution with practically zero magnetic moment ($\mu_V = 0.005\mu_B$) at V sites was obtained (cf. Fig.4).

For nocentrosymmetric $P2_1mn$ crystal structure we have two types of VO_5 alternating chains in b axis direction. Introducing an initial spin polarization on V1 and V2 sites, which correspoηds to mentioned AF-1 and AF-2 magnetic orderings, we performed the standard LSDA band calculations for these two cases also. We found that in both cases system relaxed to AF-1 solution, i. e., the self-consistent solution with antiferromagnetic order both in b and a axis direction is not possible for noncentrosymmetric structure $P2_1mn$ of NaV_2O_5. The total density of states, as well as vanadium V1 and V2 partial density of states for the majority and minority spin directions are given in Fig. 2 of our previous work devoted to this vanadate compound [32]. LSDA electronic band structure and total DOS are given in Fig. 5, for completeness. We will also repeat here the results for magnetic moments on vanadium sites $\mu_{V1} = 0.46\mu_B$, $\mu_{V2} = 0.18\mu_B$, and the band gap value of 0.2 eV. In this self-consistent calculation using the experimental atomic positions with the $P2_1mn$ symmetry, the pronounced difference of the spin density exists at two inequivalent vanadium sites suggesting some kind of partial charge redistribution and ordering.

C. LDA+U results

Electronic structure calculations of α '-NaV$_2$O$_5$ on the basis of the self-interaction corrected LDA+U method [30] were performed for the supposed AF-1 and AF-2 magnetic orderings and the same crystal structures as in the previous section LSDA calculations. Unlike the LSDA, where the stable solution produced a very small band gap and magnetic moments on both vanadium sites for AF-1 magnetic ordering and $P2_1mn$ crystal structure, the LDA+U method produced an insulating solution with the pronounced energy-gap value of 2.7 eV and the magnetic moment of $0.97\mu_B$ only on V1 type of vanadium atoms (these are inside white square pyramids in Fig. 1). The results of the LDA+U calculations of one electron energies and DOS curves are given in Fig. 5. (More complete presentation of the results for this crystal structure are given in Figs. 3(a)-3(d) of Ref. [32]).

A group of two narrow nearly degenerate topmost valence bands obtained by means of spin-restricted TB-LMTO-ASA calculations (Fig. 5), is pushed down to other valence manifold bands, when the LDA+U method is used (Fig. 5). An indirect gap of 2.7 eV is opened between T and Γ points. This gap value is in accordance with room-temperature optical absorption spectrum of α '-NaV$_2$O$_5$ single crystal obtained in [22], where an absorption edge slightly above 3 eV was supposed to correspond to the onset of a charge transfer transition across the gap. Our theoretical gap value could be taken as quite corresponding to the experiment of Golubchik *et al.* [22]. The stable self-consistent solution for the AF-2 magnetic ordering could not obtained. Namely, an initial spin polarization on V1 and V2 sites, which corresponds to mentioned AF-2 magnetic ordering, relaxed to the AF-1 ordering in noncentrosymmetric $P2_1mn$ crystal structure.

The results of the present LDA+U calculations of one electron energies and total density of states for AF-1 and AF-2 order and centrosymmetric $Pmmn$ crystal structure are given in Fig. 6. In the case of AF-1 order a direct gap of 0.68 eV is opened at T point, with the same magnetic moments at equivalent vanadium sites equal to $\mu_V = 0.6\mu_B$. Bands along the BZ symmetry lines and total DOS curve depicted in Fig. 6, except for the much smaller splitting between the V-d_{xy} spin-up and spin-down bands (two equivalent vanadim sites in this case), are very similar to the ones obtained for $P2_1mn$ crystal structure and same magnetic AF-1 order.

In the case of $Pmmn$ crystal structure and AF-2 magnetic order a gap of 0.1 eV is opened at T point and the same magnetic moments at equivalent vanadium sites equal to $\mu_V = 0.6\mu_B$ are obtained. To the best of our knowledge, this is the smallest gap opened by the LDA+U method in some transition metal oxide compound, indicating the importance of electronic correlation effects and interesting physics in this crystalline modification of vanadate α '-NaV$_2$O$_5$.

The standard LDA, LSDA and LDA+U bands of α '-NaV$_2$O$_5$ around the Fermi level are extremely similar to the respective bands of the first inorganic spin-Peierls compound CuGeO$_3$ [42,7]. It is therefore natural to presume their similar physical characteristics, i.e., the SP transition accompanied by dimerization in one- dimensional antiferromagnetic chains for the $P2_1mn$ crystal structure. The situation with the centrosymmetric $Pmmn$ crystal structure could be, according to the present investigations, more complicated and further more accurate calculations are very wellcomed.

Other features obtained by the ordinary LDA+U method when testing SP cuprate CuGeO$_3$ [7] could be seen in the earlier [32] and the present study of vanadate α '-NaV$_2$O$_5$. These are: spectral weight redistribution of V 3*d* and O 2*p* bands, important enhancement of the oxygen contribution to the top of the valence band, mainly V 3*d* character of unoccupied bands indicating a charge transfer character of the gap in this compound etc.

IV. TB MODEL

Matching of the density functional results on Hubbard and Heisenberg models yields values for the model parameters which describe the insulating behavior of NaV_2O_5 and its magnetic properties. The *Pmmn* crystal structure of the vanadate NaV_2O_5 in xy plane is given in Fig. 2. The circles denote the positions of vanadium ions, diamonds the positions of oxygen O(1) and O(2) ions which form the basal quadrangles of VO_5 pyramides oriented in ± z directions. The positions of the equivalent V1/V2 atoms located above/below the basal plane (open/shaded circles) are shown also. One can also see apex oxygens (diamonds inside circles) and interplane sodium ions (squares) in Fig. 2.

Earlier analysis of density functional theory (DFT) band states and mapping of the bands to those of TB models used the dispersion of the bonding states and only the center of gravity of antibonding states [31]. The bands around the Fermi level obtained from our TB-LMTO-ASA band calculations are predominantly of V-d_{xy} character (Fig. 3). These bands are almost the same as the respective bands obtained by Smolinski *et al.* [31] on the basis of full-potential linearized augmented plane wave method. We include in our analysis of the dispersion of DFT band states all four physically most interesting V-d_{xy} orbitals, i. e., both bonding and antibonding vanadium states.

Since there are four vanadium atoms in the paramagnetic elementary cell, in the simplest possible approach one can take only these four V-d_{xy} orbitals. This will give the 4×4 Hamiltonian, which has a dependence on a number of tight-binding parameters. We are considering here the following six parameters:

(i) $t_\perp$ - the hopping term along a rung,

(ii) $t_{||}$, $t'_{||}$ - the hopping terms between the first and the second nearest neigbours along legs of a ladder,

(iii) t_1, t_2 - the small interladders hoppings,

(iv) $t^{(2)}_{xy}$ - diagonal intraladder hopping between the rungs.

We also included the additional parameter $e_{\rm sh}$ which has to shift the model energies in order to coincide them with the LMTO determined Fermi level. Our 4×4 tight-binding Hamiltonian is of the following form:

$$H(\vec{k};\{t\}) = \begin{pmatrix} A & u & 0 & v \\ u^* & A & v^* & 0 \\ 0 & v & A & u \\ v^* & 0 & u^* & A \end{pmatrix} \tag{5}$$

where,

$$\begin{aligned} A(\vec{k};\{t\}) &= 2t_{||}\cos(k_y b) + t'_{||}\cos(2k_y b) + e_{sh} \\ u(\vec{k};\{t\}) &= \left[2t_\perp + t^{(2)}_{xy}\cos(k_y b)\right] \exp^{i\,k_x(1/2-2p)a} \equiv u_0 \exp^{i\,k_x(1/2-2p)a} \\ v(\vec{k};\{t\}) &= 2\left[t_1\cos\left(\frac{k_y b}{2}\right) + t_2\cos\left(\frac{3k_y b}{2}\right)\right] \exp^{-2i\,k_x pa} \exp^{2i\,k_z qc} \equiv v_0 \exp^{-2i\,k_x pa} \exp^{2i\,k_z qc} \end{aligned}$$

$p = 0.0979$, $q = 0.108$, $a = 3.1338\,b$, $c = 1.3284\,b$. The Hamiltonian (5) has the following eigeneneries:

$$
\begin{aligned}
E_{1/2}^{\mathrm{MODEL}}(\vec{k}) &= A \pm \sqrt{(u-v)(u^{*}-v^{*})} = A \pm \sqrt{u_0^2 + v_0^2 - 2u_0v_0\cos\left(\frac{k_xa}{2} - 2k_zqc\right)} \\
E_{3/4}^{\mathrm{MODEL}}(\vec{k}) &= A \pm \sqrt{(u+v)(u^{*}+v^{*})} = A \pm \sqrt{u_0^2 + v_0^2 + 2u_0v_0\cos\left(\frac{k_xa}{2} - 2k_zqc\right)}
\end{aligned}
\qquad (6)
$$

Only with use of the diagonal intraladder hopping parameter $t_{xy}^{(2)}$ and the next nearest neighbour transfer in the chain direction $t'_{\|}$ we were able to obtain proper shape and the separation of bonding and antibonding bands (cf. Fig. 7). Our TB parameters are given in Table 1.

In the investigation of low dimensional spin systems the knowledge of dominant magnetic interactions and their interrelation is of crucial importance. The same exchange and frustration parameters extracted from different experimental data have been quite different from each other [44]. Substances with frustrated spin interactions are not strictly governed by a traditional spin-Peierls theory as the magnetic system in these cases may show spontaneous long-range magnetic dimerization in the ground state even without any lattice dimerization. The frustration parameter obtained from our theoretical estimation is $\alpha \sim \left(t'_{\|}/t_{\|}\right)^2$=0.11. Tight-binding analysis for the most important LSDA and LDA+U bands (see Fig. 8) is needed and is the subject of our further investigations.

V. CONCLUSIONS

The results of paramagnetic LDA and antiferromagnetic LSDA functional TB-LMTO-ASA band structure calculations of orthorhombic vanadate $\alpha\,'$-NaV$_2$O$_5$, as well as LDA+U band structure results of this second inorganic compound where the spin-Peierls instability was reported [16] are presented. Our calculations are performed for both observed crystal modifications of this compound (centrosymmetric $Pmmn$ and noncentrosymmetric $P2_1mn$) and two supposed antiferromagnetic orderings with the intention of clarifying overall bonding characteristics and the possibilities and limitations of band structure methods to discriminate between quite different physical properties of these two topologically and structurally almost identical systems.

Both the LSDA and the LDA+U calculations have given two different types of vanadium atoms in the chains along orthorhombic b-axis for $P2_1mn$ crystal structure. An extremely small gap value obtained by spin-unrestricted LSDA calculations has indicated the importance of a more careful treatment of the interactions beyond the LSDA in order to obtain an appropriate quantitative description of vanadate $\alpha\,'$-NaV$_2$O$_5$. Recently suggested LDA+U method of Anisimov and *et al.* [30], was very successful in treating magnetism in many insulating compounds with pronounced electronic correlation effects behind the second Hund's rule which are responsible for orbital polarization and formation of local (atomic-like) magnetic moments.

Our results for the electronic structure of the $P2_1mn$ vanadate $\alpha\,'$-NaV$_2$O$_5$, calculated with the LDA+U method based on the potential obtained from the postulated energy functional (2), offer a significant improvement over the standard LDA and LSDA band calculations of the same system. The important features for $P2_1mn$ $\alpha\,'$-NaV$_2$O$_5$ are as follows:

(i) A stable insulating antiferromagnetic solution with the acceptable value of the vanadium local magnetic moment only on one type of vanadium atoms ($\mu_{\mathrm{V1}} = 0.97\mu_B$) is obtained.

(ii) This magnetic moment is carried almost entirely by the V1-d_{xy} orbitals which are the lowest occupied vanadium d-orbitals. Thus in the LDA+U method, d_{xy} states are strongly modified by the on-site Coulomb correlations.

(iii) An indirect charge transfer gap ($\sim$ 2.7 eV) is in agreement with the experimental value (greater than 3 eV [22]).

(iv) Hubbard type correlations and AF exchange interactions play dominant roles in the proper gap opening and the suitable description of magnetic moments on only one type of vanadium atoms in $P2_1mn$ α '-NaV_2O_5.

(v) The self-consistent solution for orthorhombic phase of α '-NaV_2O_5 described by non-centrosymmetric space group $C_{2v}^7 - P2_1mn$ could be obtained only for the supposed AF-1 antiferromagnetic order.

Based on these results, we could say that the LDA+U calculations support the picture of 'chain'-type antiferromagnetism in $P2_1mn$ structure. Namely, the charges concentrate on one leg of the ladders and the charge disproportination (charge ordering) exists. The standard spin-Peierls scenario with V^{4+} spin-1/2 chain lattice dimerization is possible in this crystal structure.

New theoretical and experimental facts show that the phase transition in NaV_2O_5 is not an ordinary SP transition (cf. Ref. [29]). In the quest for main phenomena responsible for the observed phase transition we performed the same upper mentioned band structure calculations for the centrosymmetric *Pmmn* structure of α '-NaV_2O_5 and two supposed antiferromagnetic orderings. With this goal in mind, we further present a brief discussion of the main Coulomb correlated band structure results we have obtained.

Our results for the electronic structure of the *Pmmn* vanadate α '-NaV_2O_5, calculated with the LDA+U method are as follows (for AF-1 ordering):

(i) A stable insulating antiferromagnetic solution with the local magnetic moments at equivalent vanadium sites equal to ($\mu_{\mathrm{V}} = 0.6\mu_B$) is obtained.

(ii) This magnetic moment is carried almost entirely by the V-d_{xy} orbitals which are the lowest occupied vanadium d-orbitals in accordance with the findings of Horsch and Mack [24] obtained for the same compound and in *Pmmn* crystal structure. We can see that approximately one electron is located in a bonding molecular V-O-V orbital. Coulomb correlations in the framework of the LDA+U method have modified significantly the vanadim d_{xy} states for this structure also.

(iii) The direct charge transfer gap of 0.68 eV is obtained.

(iv) Hubbard type correlations have increased noticeably the magnetic moment on vanadium sites and the insulating gap value.

Much more peculiar results are obtained for *Pmmn* structure and AF-2 magnetic ordering (antiferromagnetic order both along b and a orthorhombic axes). The LSDA calculations were unable to give magnetic and non-metallic solution for this type of ordering. The LDA+U results are quite specific also. Although we have obtained the magnetic moment on vanadim sites of $\sim 0.6\mu_B$, a gap value of only 0.1 eV was obtained. To be fully precise, we should say that both LSDA and LDA+U TB-LMTO calculations for *Pmmn* structure and AF-2 ordering converged very slowly. We have obtained self-consistent results with some relaxing of usual conditions. There exists also the unusual difference in the values of magnetic moments at equivalent vanadium sites equal to 0.03 μ_B. On the other hand, it is quite natural to expect that the vanadium atoms along the rungs of the ladders (a axis direction) are coupled antiferromagnetically, and that the difference of the electronic structure between this ordering and the ferromagnetic ordering in a axis direction is small. The interaction along the a axis is expected to be very weak [33]. The Fig. 6 of the the present work is the clear illustration of the fact that these expectations were not fulfilled. More precise and detailed band calculations are needed before one could say with confidence which magnetic structure is realized in $Pmmn$ crystal modification of α '-NaV_2O_5. Doubling the unit cell in the a and the b direction and quadrupling in the c direction (if one leans on recent experiments [35]) is computationally quite demanding.

In this paper we were able to show that the LDA+U has produced the charge ordering which is responsible for a magnetic decoupling of adjacent double chains in $P2_1mn$ α '-NaV_2O_5 [16,21], appropriate gap value, and one dimensional character of this compound observed in magnetic susceptibility measurements [16].

A recent report on a new x-ray diffraction study of the one-dimensional α '-NaV_2O_5 reveals a centrosymmetric $D_{2h}^{13} - Pmmn$ crystal structure with one type of V site [31,34], contrary to the previously postulated non-centrosymmetric $C_{2v}^{7} - P2_1mn$ structure with two types of V sites (V^{4+} and V^{5+}). This redetermination of the structure by single crystal x-ray diffraction at room temperature also shows three instead of five inequivalent oxygen positions. The topology of the structure remains essentially unchanged with respect to the previous result [17]. Due to that fact the calculated energy bands of centrosymmetric $Pmmn$ NaV_2O_5 by means of the full-potential linearized augmented plane wave method, are practically the same as our paramagnetic TB-LMTO-ASA results (one should compare our Fig. 3 with Fig. 2 of Ref. [31]).

Enormous differences in the electronic structure appear when one starts spin-unrestricted calculations of this compound in two observed crystal structures, although these differences are quite unexpected for the two topologically and structurally almost identical systems. The LDA+U method is quite capable in handling various spin orderings in NaV_2O_5.

Mapping of the density-functional results on the Hubbard and Heisenberg models yields values for the model parameters which explain successfully the insulating and magnetic properties of NaV_2O_5 [31]. Our four band model for TB analysis of paramagnetic band structure of $Pmmn$ NaV_2O_5 reveals the importance of chain frustration and diagonal intraladder hopping. To the best of our knowledge this is the first estimation of the frustration parameter obtained from some *ab initio* calculations, and the pointing to the importance of the diagonal intraladder hopping terms. Bearing in mind the importance for the model calculations of relative relations between hopping terms, directly connected with respective exchange integrals, we hope that the results for these quantities obtained in the present paper might be helpful.

The crystal structure data in Refs. [31,34] are for homogenous phase ($T > T_{SP}$). The definite crystal structure for $T < T_{SP}$ is still unsettled and has yet to be determined in detail [21,35]. Bearing that fact in mind, our band structure calculations for centrosymmetric $Pmmn$ and noncentrosymmetric $P2_1mn$ crystal structure of α '-NaV_2O_5 presented in this paper might be useful in future experimental and theoretical investigations of this interesting compound.

Concluding the paper, we could say that the LDA+U method of Anisimov *et al.* [30] gave an essentially advanced description of electronic and magnetic properties of vanadate α '-NaV_2O_5 as compared with the standard LDA and LSDA treatment of the same compound.

VI. ACKNOWLEDGEMENTS

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TABLE I. Calculated hopping terms in units of eV for the model (5).

model	$t_{\parallel}$	$t_{\perp}$	t_1	t_2	$t'_{\parallel}$	$t^{(2)}_{xy}$	$e_{\rm sh}$
present work	-0.09	-0.35	0.02	0.03	-0.03	-0.15	0.38
Ref. [31] (I)	-0.17	-0.38	0.012	0.03	–	–	–
Ref. [31] (II)	-0.17	-0.54	–	–	–	–	–
Ref. [24]	0.15	0.35	0.3	–	–	–	–

Figure captions:

Fig. 1 Crystal structure of α '-NaV$_2$O$_5$. The V^{4+}O$_5$ and V^{5+}O$_5$ pyramids running in the b axis direction are shown by the white and shaded square pyramids, respectively. The positions of Na ions between planes are shown also.

Fig. 2 Schematic representation for the supposed AF orderings used in present band calculations for $Pmmn$ structure of α '-NaV$_2$O$_5$. The circles denoted postions of equivalent V$_1$/V$_2$ ions located above/below the basal plane (open/shaded circles), diamonds the positions of the oxygen ions, and the plane projections of sodium ions (squares).

Fig. 3 V-d_{xy} bands as obtained from LDA TB-LMTO-ASA calculations for $Pmmn$ (open circles) and $P2_1mn$ (filled triangles) crystal structures, respectively.

Fig. 4 AF bands and total DOS for $Pmmn$ α '-NaV$_2$O$_5$ obtained by the LSDA method for two supposed (AF-1 and AF-2) magnetic orderings.

Fig. 5 AF bands and total DOS for $P2_1mn$ α '-NaV$_2$O$_5$ obtained by the LSDA method and the LDA+U method for AF-1 magnetic ordering.

Fig. 6 Energy bands and total DOS for $Pmmn$ α '-NaV$_2$O$_5$ obtained by the LDA+U method and two supposed magnetic orderings.

Fig. 7 Paramagnetic V-d_{xy} bands for $Pmmn$ α '-NaV$_2$O$_5$ calculated by TB-LMTO-ASA (circles) and the same bands calculated by use of TB model of Section IV (full lines).

Fig. 8 The bands around the Fermi level obtained by the LDA+U and the LSDA method for for $Pmmn$ (open circles) and $P2_1mn$ (filled triangles) structures of α '-NaV$_2$O$_5$.

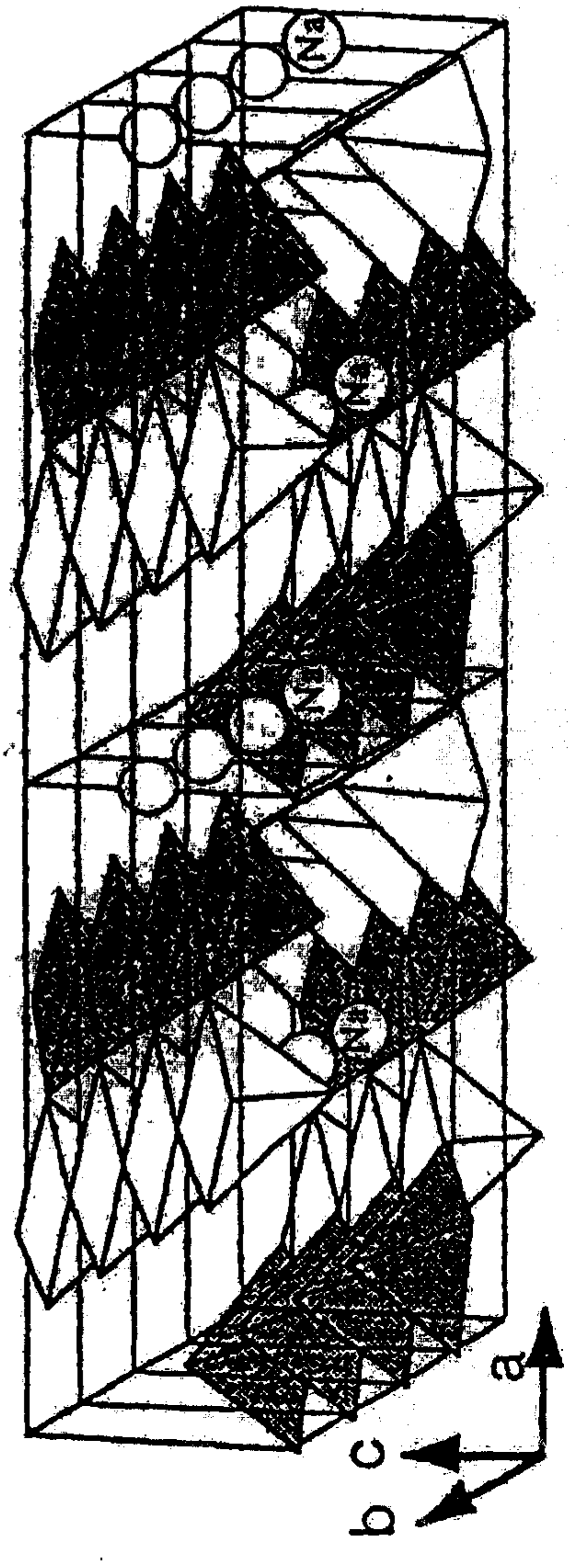

Fig. 1

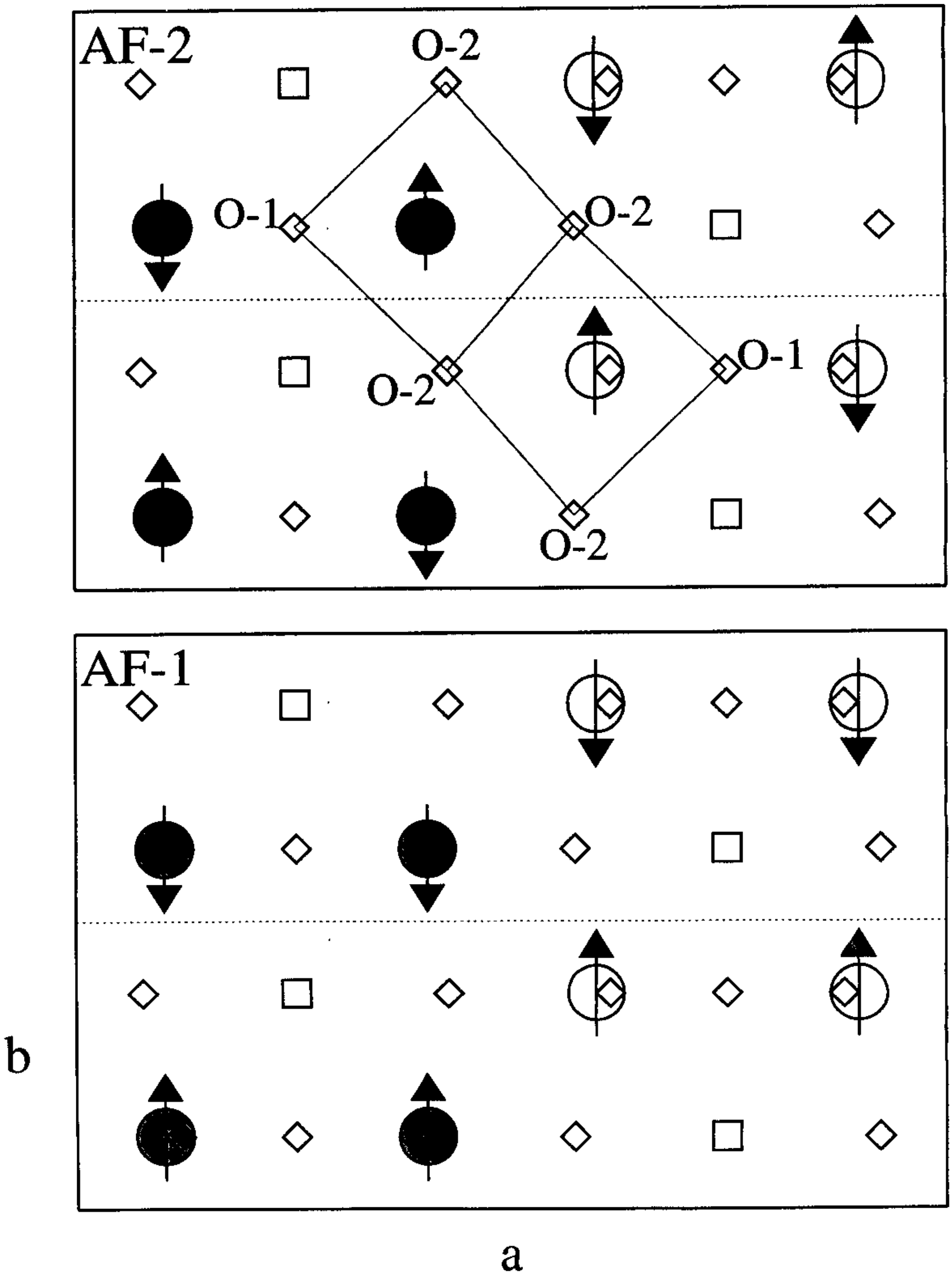

Fig. 2

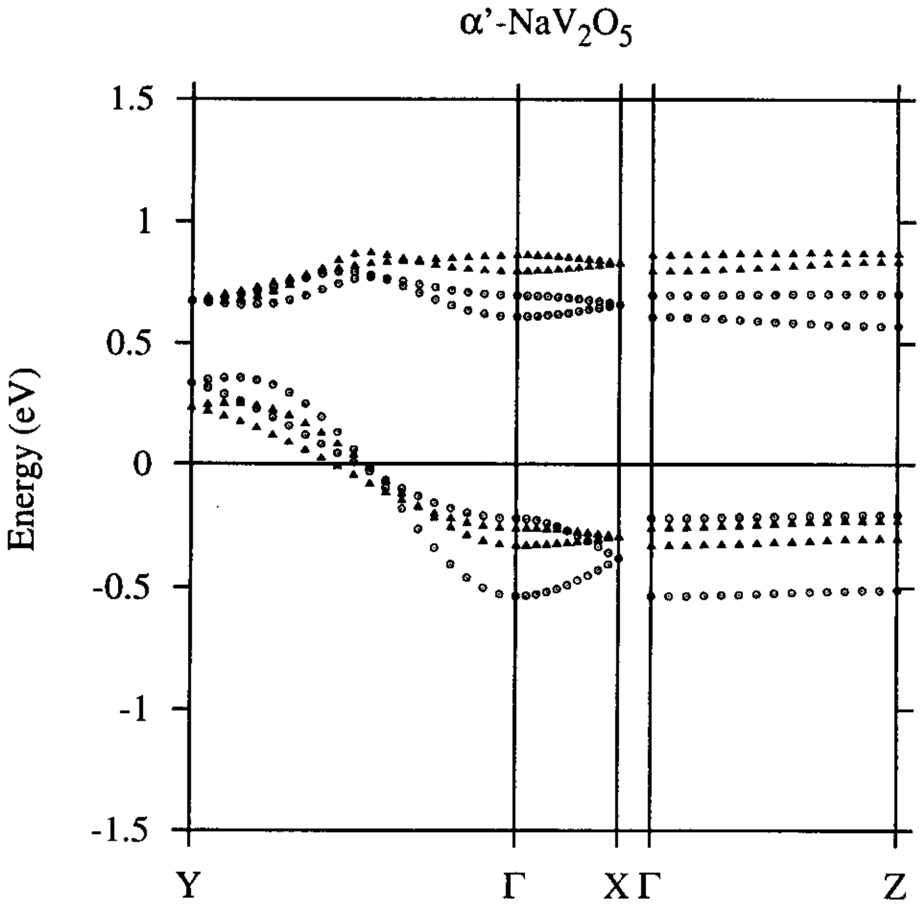

Fig. 3

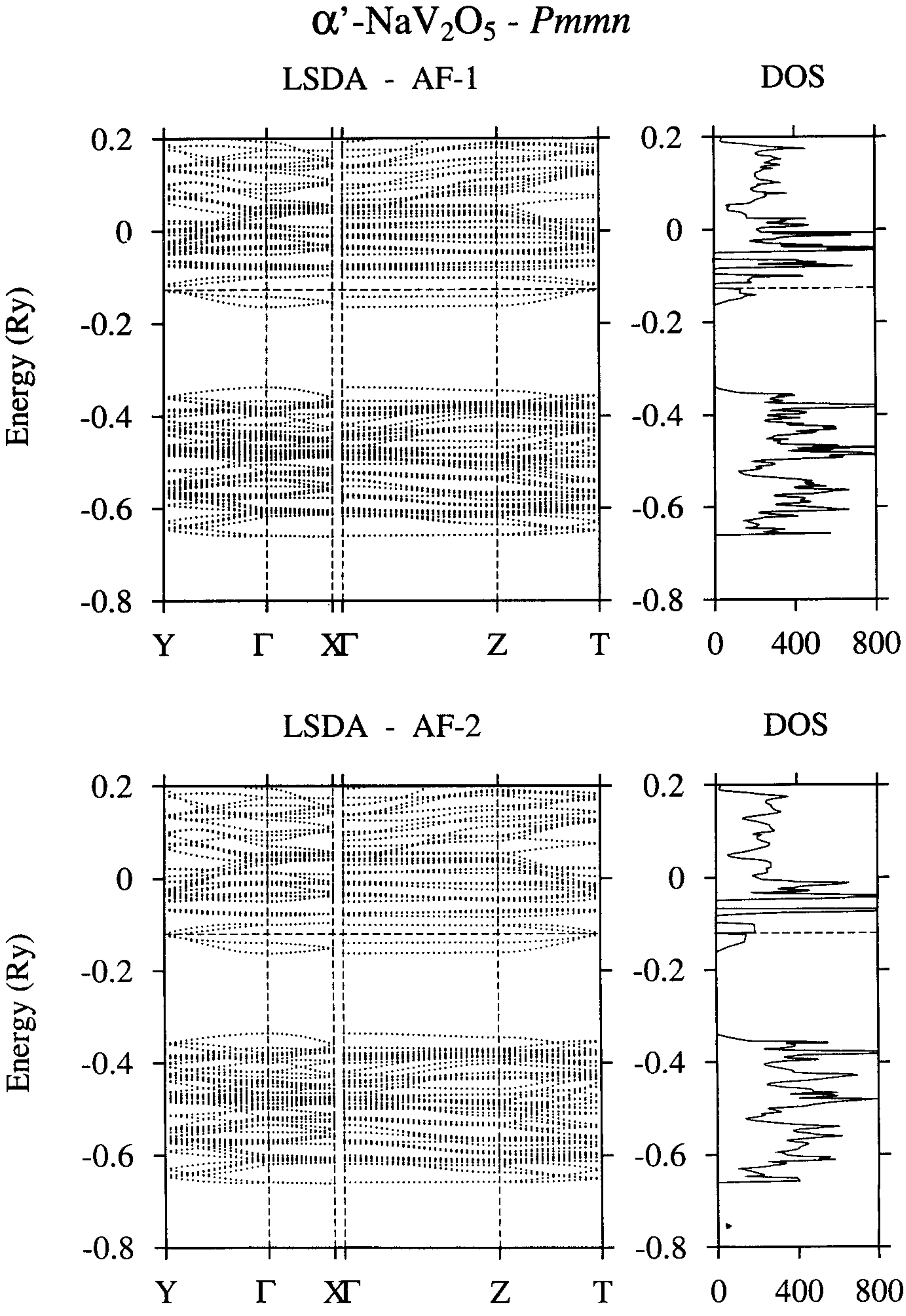
α'-NaV$_2$O$_5$ - *Pmmn*
LSDA - AF-1
DOS
Energy (Ry)
0.2
0
-0.2
-0.4
-0.6
-0.8
Y
Γ
X
Γ
Z
T
0
400
800
LSDA - AF-2
DOS
Energy (Ry)
0.2
0
-0.2
-0.4
-0.6
-0.8
Y
Γ
X
Γ
Z
T
0
400
800

Fig. 4

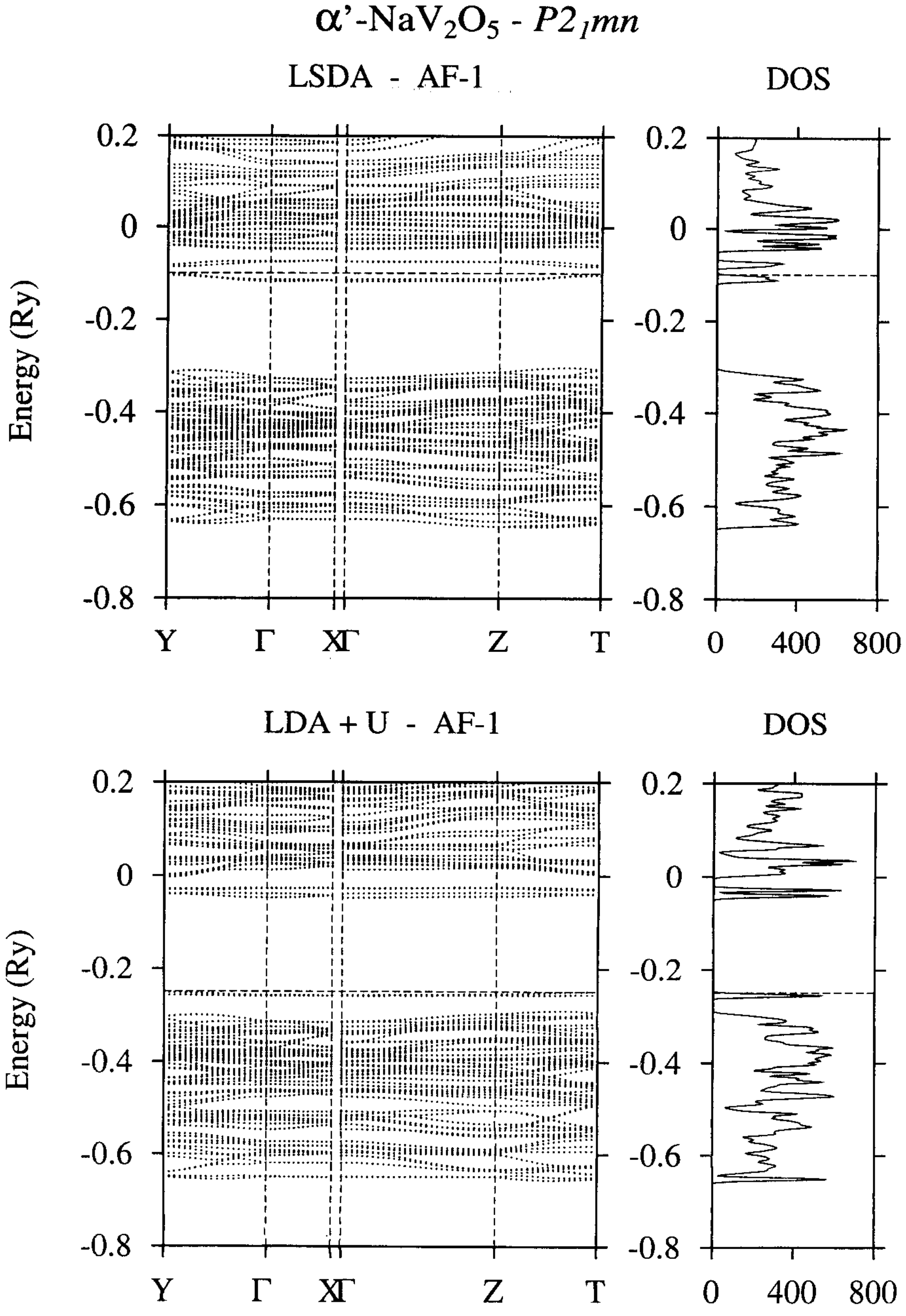
α'-NaV$_2$O$_5$ - $P2_1mn$
LSDA - AF-1
DOS
Energy (Ry)
0.2
0
-0.2
-0.4
-0.6
-0.8
Y
Γ
X
Γ
Z
T
0
400
800
LDA + U - AF-1
DOS
Energy (Ry)
0.2
0
-0.2
-0.4
-0.6
-0.8
Y
Γ
X
Γ
Z
T
0
400
800

Fig. 5

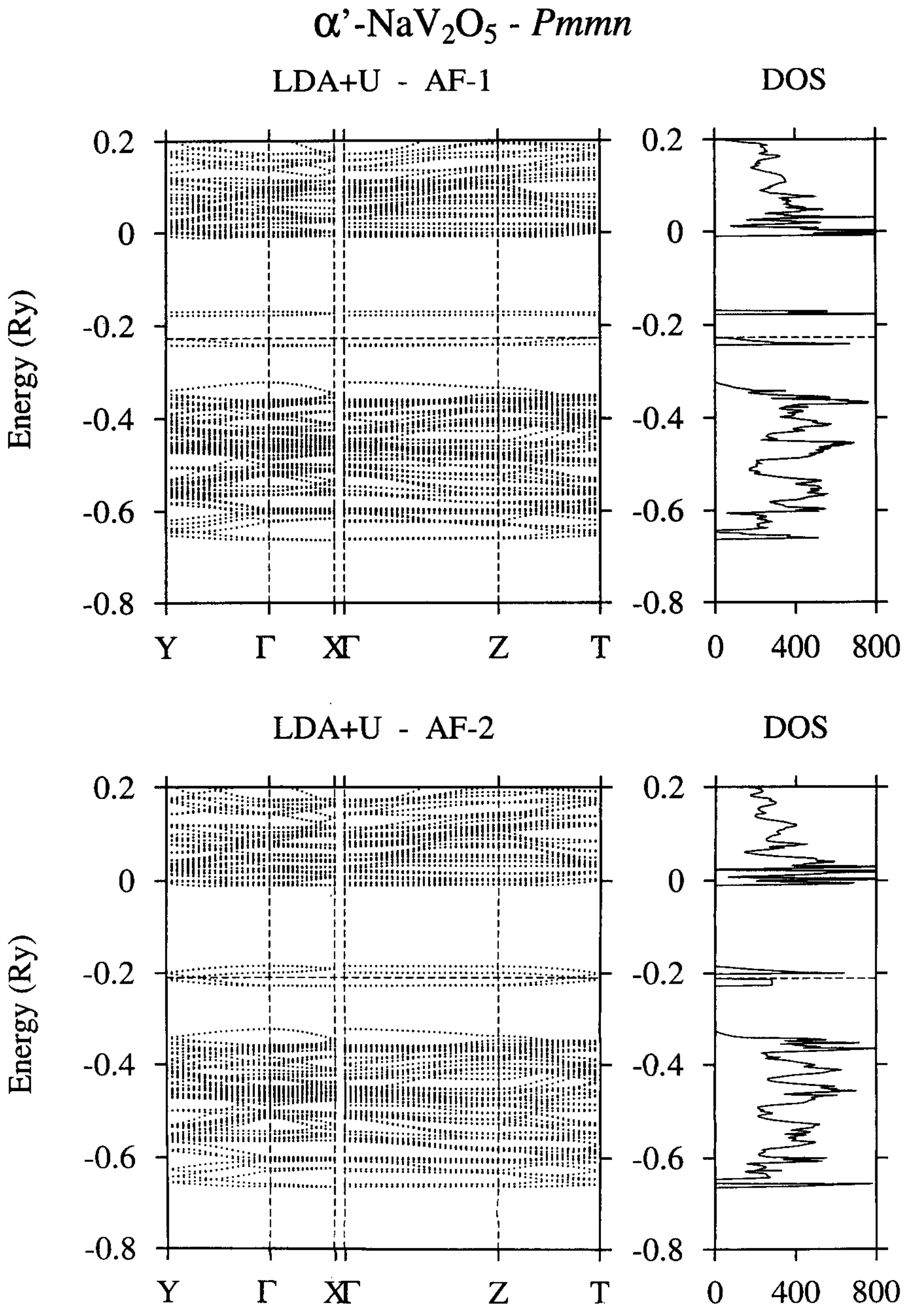
α'-NaV$_2$O$_5$ - *Pmmn*
LDA+U - AF-1
DOS
LDA+U - AF-2
DOS
Energy (Ry)
0.2
0
-0.2
-0.4
-0.6
-0.8
Y
Γ
X
Γ
Z
T
0
400
800

Fig. 6

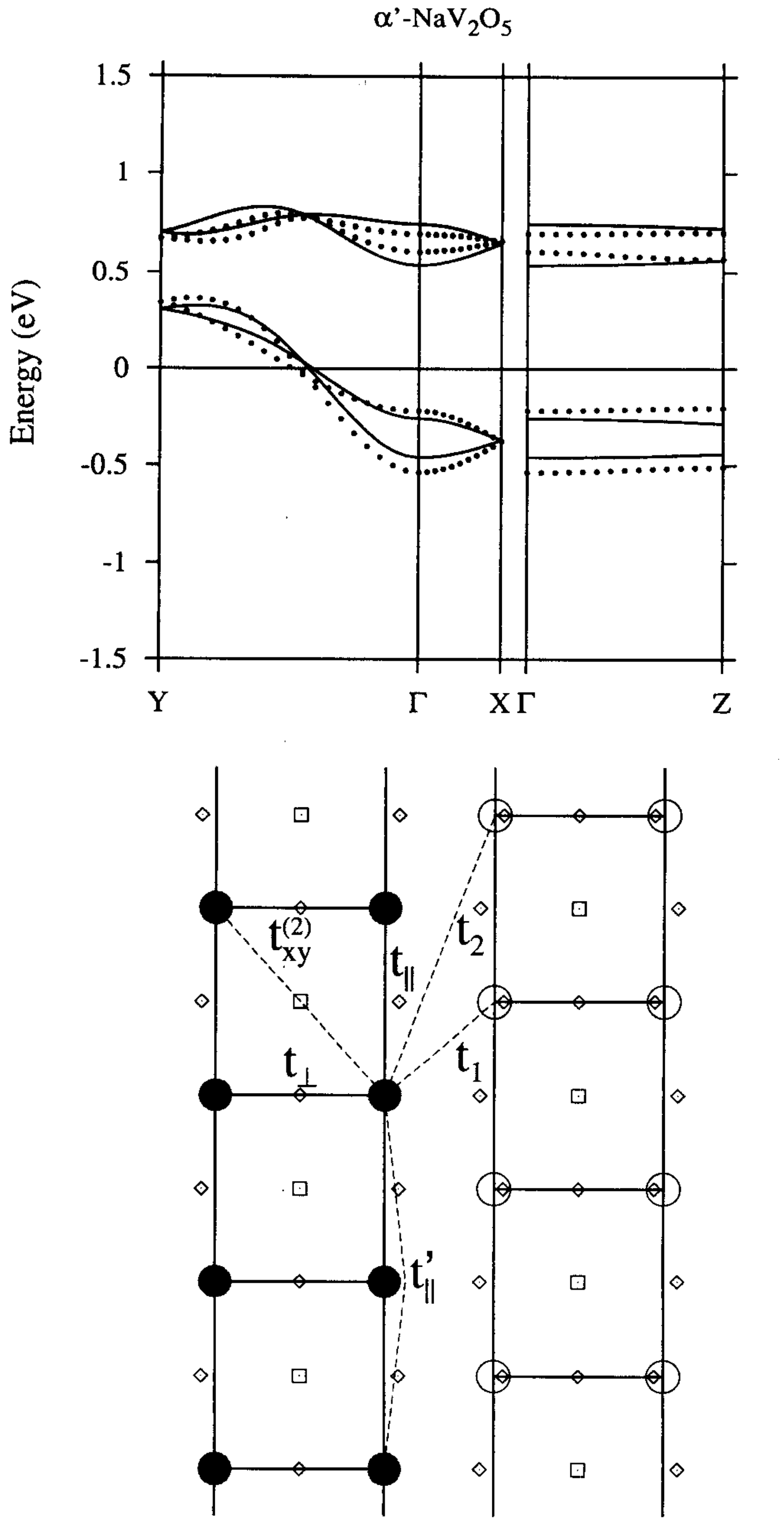

Fig. 7

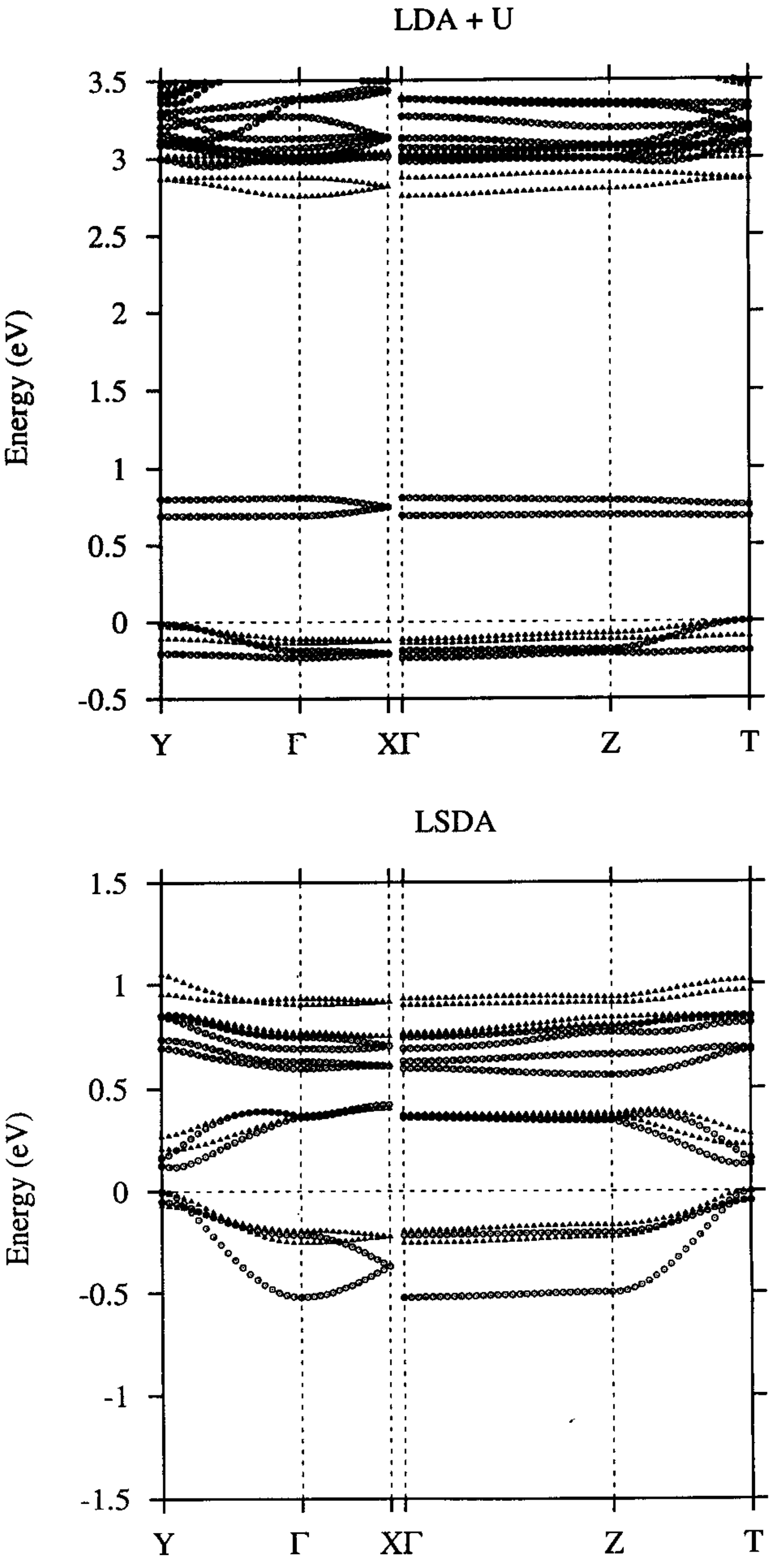
LDA + U
Energy (eV)
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
Y
Γ
XΓ
Z
T
LSDA
Energy (eV)
1.5
1
0.5
0
-0.5
-1
-1.5
Y
Γ
XΓ
Z
T

Fig. 8