

Charge-orbital ordering, magnetic state, and exchange couplings in quasi-one-dimensional V_6O_{13}

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During the last decades transition metal compounds have attracted much attention because of their intriguing low-temperature electronic and magnetic properties [1–3]. Many of them display complex types of spin, charge, and orbital orderings which are often accompanied by metal-insulator phase transitions driven by strong electron correlation effects [1–3]. In addition, the specific orbital ordering (OO) may result in the formation of the orbital-assisted spin Peierls state as, e.g., in CuIr_2S_4 and MgTi_2O_4 below the metal-insulator transition [4–6]. In La_2RuO_5 the competition between the Peierls-like and Jahn–Teller effects results in a remarkable insulator-to-insulator phase transition below ~ 160 K accompanied by the formation of the spin-singlet ground state [7].

While all these examples show either magnetic or nonmagnetic spin-singlet behaviors, it seems to be a rather rare phenomenon that a long-range magnetic order coexists with nonmagnetic spin-singlet states (at distinct sublattices). This remarkable behavior has been proposed in the low-temperature (LT) monoclinic phase of V_6O_{13} , a member of a homologous Wadsley series V_mO_{2m+1} and potential cathod material for Li-ion batteries. It is a mixed-valent system with both 4+ and 5+ V ions with a corresponding ratio 2-to-1, is a paramagnetic metal with a 2D layered crystal structure ($C2/m$ space group) and three crystallographically inequivalent vanadium sites [8]. At ~ 150 K, a first-order metal-insulator transition sets in V_6O_{13} which is accompanied by a crystal structure distortion to the monoclinic Pc phase and by a remarkable decrease of magnetic susceptibility [9, 10]. The phase transition at 150 K was interpreted as charge ordering at which the half of V^{4+} ions form spin-singlet pairs. The remaining V^{4+} ions are paramagnetic and order antiferromagnetically (AF) upon cooling below ~ 55 K.

In our paper, we study of the electronic structure, charge-orbital ordering, and magnetic properties [11, 12] of LT V_6O_{13} [8, 9] using the DFT and DFT + U (with the Hubbard $U = 3.75$ eV and Hund's exchange $J = 0.9$ eV) band-structure calculations [13, 14]. We obtain that the V ions in double layers formed by the V2a/V3a and V2b/V3b ions are aligned ferromagnetically with magnetic moments of $-0.14/ -0.84 \mu_B$ and $0.11/0.86 \mu_B$, respectively, while the layers are stacked AF along the a -axis. Moreover, the V1a and V1b sites are AF with spin moments of 0.86 and $-0.85 \mu_B$, respectively. In agreement with photoemission data [15, 16], the DFT + U calculations result in an opening of the energy gap of 0.2 eV. The occupied V 3d states are strongly localized and form two well defined bands below the Fermi level and in the energy range between -2 and -0.6 eV, consistent with the recent ARPES results [15, 16].

We note that the self-consistent solution obtained by DFT + U is charge and orbitally ordered. The integrated charge state of the V 3d bands in the energy range between -2 eV and the Fermi level indicates formation of the t_{2g} charge and orbital ordered state in which one of the V1 and V3 ions each has one t_{2g} orbital occupied, whereas all the V2 t_{2g} orbitals are empty. According to this we label the V1 and V3 as 4+ ($3d^1$), and V2 as 5+ ($3d^0$) V ions. This suggests that the bands near E_F are derived from the zigzag chains with mixed 4+ and 5+ V sites [15, 16]. Moreover, the V 3d occupations exhibit the $d_{xz\uparrow}/d_{xy\downarrow}$ character for the occupied V1a/V1b ions which are almost completely filled with the occupation number of ~ 0.8 (see Fig. 1). The occupied V3a/V3b states are predominantly of the d_{yz} character with population of $0.8 \bar{e}$. On the other hand, the remaining two t_{2g} orbitals of the V1 and V3 ions have a significantly smaller population of about 0.2. In contrast, the V2a/V2b 3d orbitals do not reveal any orbital polarization. Moreover, the V2a/V2b t_{2g} orbital

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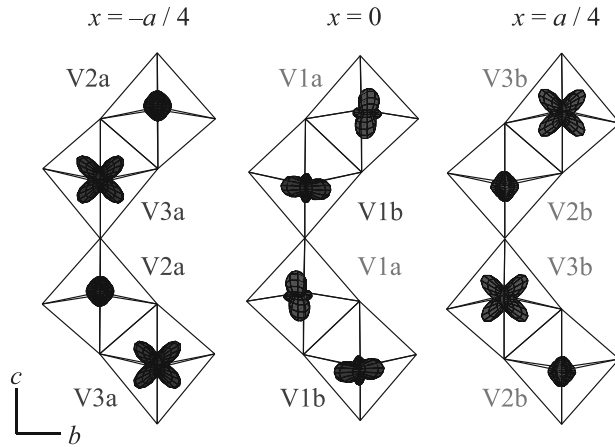


Fig. 1. (Color online) Lattice structure and orbital order projected on the (100) plane of LT V_6O_{13} . Red and blue colors correspond to the majority and minority spin, respectively

occupancies do not exceed 0.27 resulting in a remarkable charge disproportionation within the t_{2g} subshell between the V1/V3 and V2 ions. Interestingly that due to considerably larger hybridization between the O $2p$ and V2a/V2b $3d$ states the corresponding $3d$ charge disproportionation inside the atomic spheres of the V1/V3 and V2 ions is rather small, consistent with previous estimates for charge-ordered transition metal oxides.

Our analysis of exchange couplings of LT V_6O_{13} (using the Green's function method within DFT + U) [14] suggests a relatively weak interlayer coupling, less than 85 K between the V1–V2 sites. In the double V-V layer ($x = \pm a/4$) the exchange couplings in the zigzag chain (along the b -axis) are rather weak and ferromagnetic (~ 20 – 30 K), whereas the inter-chain exchanges are remarkably large and dominant (~ 220 – 348 K). In the single layer the V $4+$ ions form a sawtooth-like spin- $1/2$ zigzag chains along the b -axis which are (relatively) weakly coupled to each other. The base-base exchange coupling in the Δ -chain between the d_{xy} orbitals (ferro-orbitally ordered) on the neighboring V1b sites is large and AF (~ -420 K). Its amplitude is considerably larger than the mean base-vertex coupling (~ -280 K), i.e., a ratio between the base-base and mean base-vertex couplings in the V1 Δ -chain is smaller than the upper critical value of 1.53, below which the spin gap state occurs in the sawtooth lattice [17]. Based on this we conclude on the formation of the orbital-assisted spin-Peierls state in the single V-V layer of the system [18]. Our result agrees well with the analysis of the crystal structure below the phase transition at 150 K.

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1. M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
2. E. Dagotto, *Science* **309**, 257 (2005).
3. S. V. Streltsov and D. I. Khomskii, *Phys.-Uspekhi* **60**, 1121 (2017).
4. D. I. Khomskii and T. Mizokawa, *Phys. Rev. Lett.* **94**, 156402 (2005).
5. P. G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R. M. Ibberson, Y. Koyama, Y.-S. Hor, V. Kiryukhin, and S.-W. Cheong, *Nature (London)* **416**, 155 (2002).
6. M. Schmidt, W. Ratcliff, II, P. G. Radaelli, K. Refson, N. M. Harrison, and S. W. Cheong, *Phys. Rev. Lett.* **92**, 056402 (2004).
7. P. Khalifah, R. Osborn, Q. Huang, H. W. Zandbergen, R. Jin, Y. Liu, D. Mandrus, and R. J. Cava, *Science* **297**, 2237 (2002).
8. K. A. Wilhelmi, K. Waltersson, and L. Kihlberg, *Acta. Chem. Scand.* **25**, 2675 (1971).
9. K. Kawashima, Y. Ueda, K. Kosuge, and S. Kachi, *J. Cryst. Growth.* **26**, 321 (1974).
10. S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanazaki, A. Fujimori, H. Daimon, Y. Ueda, K. Kosuge, and S. Kachi, *Phys. Rev. B* **41**, 4993 (1990).
11. T. Toriyama, T. Nakayama, T. Konishi, and Y. Ohta, *Phys. Rev. B* **90**, 085131 (2014).
12. Y. Shimizu, S. Aoyama, T. Jinno, M. Itoh, and Y. Ueda, *Phys. Rev. Lett.* **114**, 166403 (2015).
13. O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
14. A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B* **52**, R5467 (1995).
15. R. Eguchi, T. Yokoya, T. Kiss, Y. Ueda, and S. Shin, *Phys. Rev. B* **65**, 205124 (2002).
16. S. Suga, A. Shigemoto, A. Sekiyama, S. Imada, A. Yamasaki, A. Irizawa, S. Kasai, Y. Saitoh, T. Muro, N. Tomita, K. Nasu, H. Eisaki, and Y. Ueda, *Phys. Rev. B* **70**, 155106 (2004).
17. F. Becca, F. Mila, and D. Poilblanc, *Phys. Rev. Lett.* **91**, 067202 (2003).
18. I. Leonov, A. N. Yaresko, V. N. Antonov, U. Schwingenschlögl, V. Eyert, and V. I. Anisimov, *J. Phys. Condens. Matter* **18**, 10955 (2006).