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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 cristallographycally 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 $\sim$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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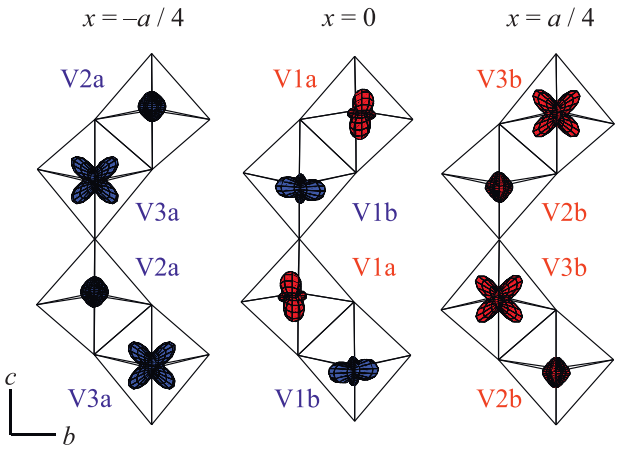

Fig. 1. (Color online) Lattice structure and orbital order projected on the (100) plane of LT V_6O_{13}. Red and blue colors correspond to the majority and minority spin, respectively

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 then 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 ($\sim$ 20–30 K), whereas the inter-chain exchanges are remarkably large and dominant ($\sim$ 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 (ferroorbitally 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. Kihlborg, 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. Kanzaki, 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).