

HEITLER–LONDON INSULATORS IN NEW OXIDE SYSTEMS

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The tight-binding band structure of AV_2O_5 systems (A is alkali element) is studied by taking into account the electron correlations in the framework of the Hubbard-like model. The evaluated band gaps, energy dispersion relations and density of electronic states are in good agreement with available experimental data. The correlated band gap provides the insulating state of the high-temperature phase. For the best studied α' - NaV_2O_5 the low-temperature phase earlier misinterpreted as the spin-Peierls state, is governed, in fact, by an opening of the Coulomb gap. Due to the nature of the correlated energy the story supports the idea to give the name *Heitler–London insulators* to $A^+V_2O_5$ compounds.

Since the discovery of a spin-Peierls behavior in quasi-1D $CuGeO_3$ there were a lot of efforts to find out similar effects in other inorganic materials. The AV_nO_{2n+1} family (A \equiv alkali or alkali earth element) has been quite perspective in that respect. In the best studied α' - phase of NaV_2O_5 the opening of a spin gap $\Delta_0 \sim 80\text{--}100$ K at $T_c \sim 34\text{--}36$ K was attributed firstly to a spin-Peierls transition [1, 2]. At present it has become evident, that this scenario is not adequate for the description of the available experimental data (e.g., [3–5]).

The presented approach is based on the hypothesis that the α' - NaV_2O_5 properties are governed by the electron correlations $U \gg t_a$ (intra-rung/dimer electron hopping integral) $> t_b$ (an electron hopping along legs in crystal b -direction) $> t_d$ (the hopping along ladder diagonals) $> t_{xy}^{bc, bm, qm}$ (interdimer hoppings between vanadium ions on the nearest ladders) (Fig. 1). According to the standard tight-binding method ($U = 0$) in solids for solving the Schrödinger

equation the eigenfunctions of the problem are constructed on the basis of the electron eigenfunctions of the isolated atoms, i.e., a conventional tight-binding method is the more suitable the greater interatomic distances in the crystal. But in this case the prevailing term in the Hamiltonian is strong electron-electron repulsion, U , which cannot be reduced to the mean field and then the problem is beyond the scope of the conventional Slater–Koster scheme at all.

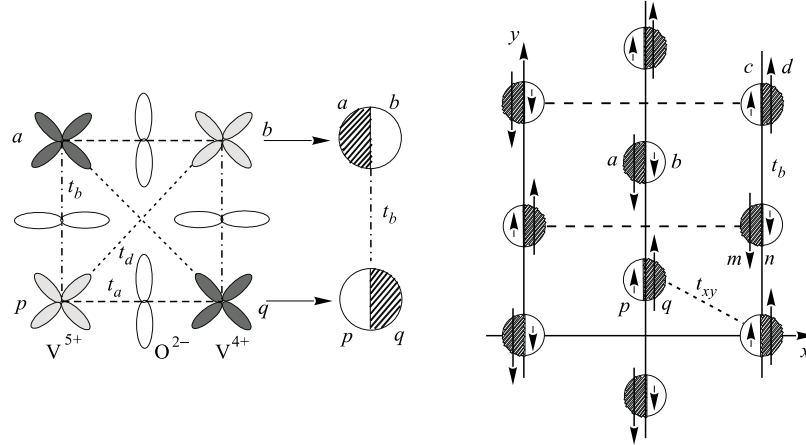


Fig. 1. The schematic view of α' - NaV_2O_5 . Each dimer/rung is replaced by a circle. The inter(intra)dimer hopping t_b (t_a) in the b (a)-direction is set along the y (x)-axis. The distances at room temperature between the nearest V-ions on neighboring dimers/rungs are 3.04 \AA and the leg constant is 3.61 \AA . The dimer size is 3.44 \AA . Oxygen p -wave functions (opened) enhance the hopping t_d along ladder diagonals. For $T > T_c$: the orthorhombic unit cell with two dimers is shown in lower panel. For $T < T_c$: the size of arrows (lower panel) reflects the charge disproportionation $\Delta n = n_{a,d,m,q} - n_{b,c,n,p}$ in the monoclinic unit cell; the shaded portions have a zigzag order

Reasonable simulation of the many-body effects is impossible in terms of the Fermi operators which are c -numbers. The necessity to introduce in this case the operators with more complicated permutation relations was indicated by Bogoliubov when developing the polar theory of metals already in 1949 year [6]. The applied technique [7] for the generalized Okubo-Hubbard X-operators in the superalgebra approach considers the tunneling part of any correlated Hamiltonian as perturbation with respect to strong electron correlations included in eigenvalues of the unperturbed part of Hamiltonian. The Hamiltonians with correlated electrons are rewritten in terms of basis and only basis vectors of corresponding superalgebra. The perturbation theory is based on the generalized Wick's theorem as an iteration procedure reducing the time-ordered product of n of X-operators to the product of $n - 1$ of thereof. The first order self-energy is the tunneling matrix itself from the perturbation Hamiltonian.

Here in the framework of the $su(2, 2)$ superalgebra approach for $A^+V_2O_5$ systems we will neglect the effects of the scattering of correlated electrons at the spin and charge fluctuations, aiming at comparing the correlated electron spectra with the conventional tight-binding results which are done in the first order of the transfer energy. In the considered order of the perturbation theory we will concentrate on the influence of band structure effects which are of significance for multicomponent systems such as AV_2O_5 .

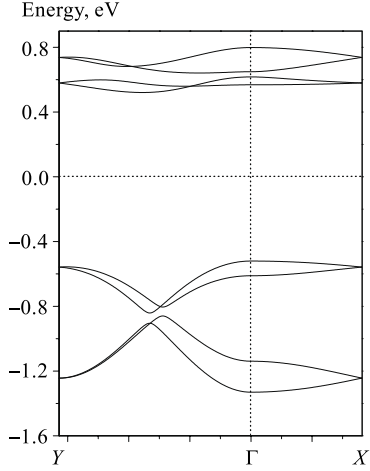


Fig. 2. The high-temperature ($T > T_c$) electron density of states in α' - NaV_2O_5 for parameters $t_a = 0.35$ eV, $t_b = 0.15$ eV, $t_d = 0.1$ eV, $t_{xy} = 0.06$ eV, $U = 4$ eV (i.e., the effective value $I \simeq 0.6$ eV) as a function of dimensionless energies $\xi / (t_b + t_d)$, $E_F = 0$ (main panel). The inset shows the density of states for noninteracting bonding electrons

allows one to consider spinless electrons. The energy dispersions are plotted in Fig. 2. The Coulomb gap Δ_C is provided by the zigzag order $\mp \varepsilon$ (Fig. 1), parameters $t_{a,d}$ and competing interdimer hops $t_{b,xy}$. The critical value $V_c \sim 0.02$ eV [9] corresponds to our threshold ε_c ($t_{xy} = 0.06$ eV, $\delta = 0.01$ eV) to trigger the phase transition. For realistic $t_{a,b,d,xy}$ and ε the so-called «spin-Peierls» phase transition occurs at $T_c = 35$ K (Fig.2). At small interladder hoppings the Coulomb gap is

Angular part of d_{xy} -wave functions provides the layerness of α' - NaV_2O_5 and the small ratio r_B/a (a is a lattice constant and r_B is the V-ion Bohr radii) enables to calculate transfer integrals as power series of $(r_B/a)^2$. Their estimates show the strong influence of a V-ion core on an electron hopping and we will distinguish the t_{xy} magnitudes at $T < T_c$: $t_{xy}^{bc} = t + \delta$, $t_{xy}^{bm} = t$, $t_{xy}^{qm} = t - \delta$. Our main strategy is developed starting from the assumption that the quarter-filled dimers V_2 form an ideal triangular lattice in the layer of VO_5 pyramids (Fig. 1). Below T_c α' - $NaV_2^{4+/5+}O_5$ is in an ordered valence phase whereas above T_c it is in a mixed valence state. Phase transition seems to be similar to the Verwey transition at $T_V \sim 120$ K in magnetite $FeFe_2^{2+/3+}O_4$ [8] with the charge ordered $Fe^{2+/3+}$ ($3d^{6/5}$) octahedral sites at $T < T_V$.

Below T_c the d_{xy} -electrons acquire the on-site energies in a monoclinic unit cell, $\varepsilon_{a,d,q,m} = -\varepsilon_{b,c,n,p} \equiv -\varepsilon$, influenced by neighboring Coulomb repulsion $V^{4+\Delta n/5-\Delta n}$: $\varepsilon = -V\Delta n$. Sites a, b, m, n and p, q, c, d have spin projections *down* and *up*, respectively.

This situation, in parallel with $U \gg t_{a,b,xy}$,

$$\Delta_C = \sqrt{\varepsilon^2 + (t_a + 2t_b)^2} + \sqrt{\varepsilon^2 + (t_a - 2t_b)^2} - 4t_d. \quad (1)$$

Its estimated magnitude $\Delta_C \approx 1$ eV (see Fig. 2) for disproportionation $\Delta n = 0.8$, $V = 0.8$ eV [10], $t_a = 0.35$ eV, $t_b = 0.15$ eV, $t_d = 0.1$ eV corresponds to the observed strong absorption of the light [11]. Eq.(1) is the extension of the splitting in terms of the «charged-magnon» scenario used in Refs. 11, 12 for a single $V^{4+} - V^{5+}$ rung ($t_{b,d} = 0$).

Above T_c the tight-binding energy bands are split due to the electron correlations as

$$\begin{aligned} \frac{\xi_p^+}{t_b + t_d} &= \varepsilon_p^\pm + \frac{1}{2} \sqrt{\left(\frac{I}{t_b + t_d}\right)^2 + 4(\varepsilon_p^\pm)^2}, \\ \frac{\xi_p^-}{t_b + t_d} &= \varepsilon_p^\pm - \frac{1}{2} \sqrt{\left(\frac{I}{t_b + t_d}\right)^2 + 4(\varepsilon_p^\pm)^2}, \end{aligned} \quad (2)$$

where dimensionless tight-binding noncorrelated energies are

$$\varepsilon_p^\pm = -\cos p_y \pm 2t \cos \frac{p_y}{2} \cos \frac{p_x \sqrt{3}}{2} \left(t = \frac{t_{xy}}{2(t_b + t_d)} \right). \quad (3)$$

The correlated band gap

$$\Delta_g = \frac{1}{2} \left[\sqrt{I^2 + 4t_b^2} + \sqrt{I^2 + 4(t_b + t_{xy})^2} \right] - 2t_b - t_{xy}, \quad (4)$$

is governed by the on-dimer repulsion for bonding electrons

$$I = 2t_a + U/2 \left[1 - \sqrt{1 + (4t_a/U)^2} \right].$$

If it were metallic carriers, the ε_p^- and ε_p^+ would have provided the quasi-2D saddle and the quasi-1D saddleless portions of the Fermi surface. Therefore it would be quite interesting to investigate the doped oxides, e.g., $\text{Na}_{1-x}\text{Ca}_x\text{V}_2\text{O}_5$, $\text{Na}_{1-x}\text{V}_2\text{O}_5$. For noncorrelated energies the partial densities of electronic states

$\rho(\varepsilon)$ have an explicit form

$$\begin{aligned}
\rho(-1-2t \leq \varepsilon^- \leq -1) &= \frac{4}{\pi^2 \sqrt{kt}} K(q), \\
\rho(-1 \leq \varepsilon^- \leq -1+2t) &= \frac{4}{\pi^2 \sqrt{kt}} F\left(\arcsin a \sqrt{\frac{2t}{(1+\varepsilon)k}}; q\right), \\
\rho(-1+2t \leq \varepsilon^- \leq 1) &= \frac{4}{\pi^2 q \sqrt{kt}} K\left(\frac{1}{q}\right); \\
\rho(-1 \leq \varepsilon^+ \leq -1+2t) &= \frac{4}{\pi^2 \sqrt{kt}} F(\arcsin a; q), \\
\rho\left(-1+2t \leq \varepsilon^+ \leq \frac{1}{2}+t\right) &= \frac{4}{\pi^2 q \sqrt{kt}} F\left(\arcsin \frac{1}{a}; \frac{1}{q}\right)
\end{aligned} \tag{5}$$

via elliptic integrals F and K of the first kind with $q = \sqrt{[2t(t+k) + 1 - \varepsilon^2]/kt}/2$, $a = \sqrt{(1+\varepsilon)(t+k)k/[2t(t+k) + 1 - \varepsilon^2]}$, where $k = \sqrt{t^2 + 2(1-\varepsilon)}$. The main panel of Fig. 3 displays the density of correlated electron states, $\rho(\xi)$, with a gap Δ_g . In a limiting noncorrelated case, the $\rho(\varepsilon)$ (inset) reproduces the essentials of the first principle computations [13]. Logarithmic divergencies inside the band are clear manifestations of the 2D electronic structure. We would like to emphasize that in the 1D case ($t_{xy} \rightarrow 0$) the divergencies are square-root like and they are located at the band edges $\varepsilon = \pm 1$ (noncorrelated case).

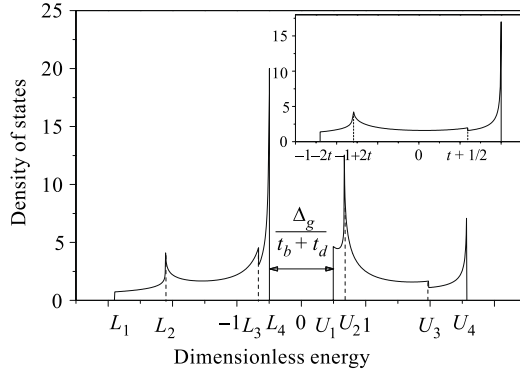


Fig. 3. The tight-binding energy dispersions for correlated d_{xy} -electrons in α' - NaV_2O_5 below T_c for parameters $t_a = 0.35$ eV, $t_b = 0.15$ eV, $t_d = 0.1$ eV, $t_{xy}^{bm} = 0.06$ eV, $t_{xy}^{bc, qm} = t_{xy}^{bm} \pm \delta$ ($\delta = 0.01$ eV) and $\varepsilon = V\Delta n$ ($V = 0.8$ eV, $\Delta n = 0.8$). Momenta are given in units $|p_x \sqrt{3}| = |p_y| = \pi$ of the Brillouine zone boundaries, the Fermi energy, $E_F = 0$, is inside the Coulomb gap $\Delta_C = 1$ eV

In summary, the analysis of the α' – NaV_2O_5 band structure leads to the conclusion about its pronounced 2D features. *The phase transition at T_c is shown to be not a spin-Peierls type but rather it is connected with the opening of the Coulomb gap in the electronic spectrum.* At $T > T_c$ the character of the insulating phase has been identified with a correlated band gap.

By virtue of the fact, that nature of the correlated energy (see Eq. (4)) is connected with the Heitler–London valence band state, our study supports the earlier proposal [5] to give the name *the Heitler–London insulators* to such systems as $\text{A}^+\text{V}_2\text{O}_5$, whereas the $\text{A}^{2+}\text{V}_2\text{O}_5$ materials are the Mott–Hubbard insulators. The presented description (also [14]) of the dimerized quarter-filled compounds, namely first members of $\text{AV}_n\text{O}_{2n+1}$ oxides, in terms of the Hubbard-like model opens new possibilities to study a variety of their properties in terms of strongly correlated electron picture.

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