

Yu. Skorenkyy, O. Kramar, Yu. Dovichyaty

Strong correlation effects in vanadium oxide films

Ternopil Ivan Puluj National Technical University, Ternopil, Ukraine, skorenkyy@mtu.edu.ua

In the present work the metal-insulator transition in doubly orbitally degenerated model of quasi-two-dimensional material based on V_2O_3 film, in which a crucial role is played by on-site Coulomb interaction and correlated hopping of electrons, has been investigated. With use of a projection procedure in the Green function method the energy spectrum of electrons has been calculated to model variations of the material properties at the temperature changes, the external pressure application and doping.

The obtained expressions for thermodynamic potential and the energy gap widths allow analyzing the possible phase transitions in a system, the dependency of characteristics on the external actions for this strongly correlated material.

Keywords: Metal-Insulator Transition, Strong Electron Correlations, Energy Spectrum.

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Introduction

Despite more than half a century of studies of the metal-insulator transition (MIT) and magnetic phase transitions in pure and doped vanadium oxides (see [1] for a review), these compounds attracted much attention recently. After the first experimental research [2], where phase diagram of doped V_2O_3 was explored, theorists proposed various models and mechanisms to explain the electrical and magnetic properties of these materials [3-7]. Most of these models took into account the Mott-Hubbard mechanism. Until 2000, the filling of 3d V-orbitals (vanadium) for different phases of vanadium oxides had never been measured by direct methods, although these values were the starting assumptions for the formulation of different theoretical models. MIT temperatures in V_2O_3 and VO_2 are 150 K and 200-300 K respectively, which values are 40 - 20 times lower than the energy gaps, 0.66 eV and 0.3-0.5 eV [8-11].

Recently, completely new properties of these well studied compounds have been discovered and these findings suggest new applications of these systems [3], in particular, as thin film devices with controlled phase transitions. New experiments have shown that the spin of vanadium atoms in V_2O_3 is equal to one [11] and a model which takes into account the orbital degeneracy of

energy levels is required to describe MIT in this compound. Such a model has been studied in [12] within the LDA + DMFT (QMC) approximation. In this work, realistic critical values of the intra-atomic Coulomb interaction U were obtained and the calculated spectrum reproduced the experimental data, in contrast to the simpler LDA method. It could be assumed that the theory of MIT in V_2O_3 has been completed however, recently intensive research of nanosystems began for the design of novel electronic devices. New results obtained for thin films of transition metals oxides have significantly raised the interest to vanadium oxides, primarily to V_2O_3 and VO_2 . In 2010, the inhomogeneity of the metallic phase at submicron level was discovered [13]. At temperature decrease in Cr-doped V_2O_3 the appearance of metallic domains in the dielectric environment has been observed, and the application of the external pressure was shown to stabilize the homogeneous metallic phase. The effect of structural disorder in V_2O_3 and VO_2 has been studied in [14] by irradiating samples with oxygen ions. At a slight irradiation of V_2O_3 , the insulating phase quickly turns into a metallic one. On the contrary, in VO_2 much more intensive (by an order of magnitude) irradiation and the corresponding increase in lattice defects number weakly affect the gradual decrease in the resistance of the insulating sample. This indicates that the electronic

correlations in V_2O_3 are long-range (magnetic ordering) and in VO_2 these correlations are local (Mott-Hubbard ones). Note that MIT in VO_2 has never been attributed to the Mott-Hubbard mechanism because of the simultaneous structural phase transition. In an earlier experimental work [15] it was shown that in VO_2 during MIT a metallic phase appears first and only then a structural phase transition occurs. This can be considered a confirmation of the Mott-Hubbard character of MIT in VO_2 and an example proving that ultrafast spectroscopy allows new insights into the complex processes associated with MIT. Along with the experimental work, there were many theoretical studies attempting explanations of the new experimental features of MIT in vanadium oxides. For example, in [16] a modified degenerate Hubbard model is considered, which allows the study of MIT induced by an electric field. The paper shows the possibility of the existence of an intermediate metastable metal phase. We should single out the work [17] in which by the method of controlled epitaxial

deformation the intermediate electronic and optical properties of thin films of pure and chromium-doped V_2O_3 have been stabilized in intermediate states between metallic and insulating phases (which is impossible to realize in bulk samples). In-plane lattice constant in this study has been tuned to control the properties of the material. These results open new prospects for the creation of electronic devices based on Mott-Hubbard narrow band systems.

I. The model Hamiltonian for vanadium oxide film

We start from the partial case of the doubly orbitally degenerate model [18, 19] suitable for description of vanadium d -electron subsystem, which takes into account the essential peculiarities of narrow energy bands

$$H = (E_d - \mu) \sum_{i\gamma\sigma} c_{i\gamma\sigma}^+ c_{i\gamma\sigma} + U \sum_{i\gamma} n_{i\gamma\uparrow} n_{i\gamma\downarrow} + U' \sum_{i\sigma} n_{i\alpha\sigma} n_{i\beta\bar{\sigma}} + (U' - J_H) \sum_{i\sigma} n_{i\alpha\sigma} n_{i\beta\sigma} + \sum_{ij\gamma\sigma} \left(t_{ij}(n, \bar{u}) + t_{ij}^a(n_{i\gamma\bar{\sigma}} + n_{j\gamma\bar{\sigma}}) + t_{ij}^b(n_{i\gamma\bar{\sigma}} + n_{j\gamma\bar{\sigma}}) \right) c_{i\gamma\sigma}^+ c_{j\gamma\sigma} + \sum_{\vec{q}f} \hbar\omega_f(\vec{q}) b_{\vec{q}f}^+ b_{\vec{q}f} + \frac{1}{2} NV_0 C \bar{u}^2. \quad (1)$$

The model energy parameters and the corresponding processes are illustrated by fig. 1. Oxygen atoms are not shown, however we note that electron hoppings between vanadium ions in V_2O_3 lattice are mediated by the oxygen sites, so the hopping parameters implicitly include the overlapping of wave functions on V and O sites and can be affected by the structural disorder substantially. We use the standard notations of the second quantization approximation [20], with c -operators of creation and annihilation of an electron with spin σ at orbital γ (α or β) of a site, electron number operator $n_{i\gamma\sigma} = c_{i\gamma\sigma}^+ c_{i\gamma\sigma}$ and b -operators for creation and destruction of phonons. For the doubly degenerated band, three different electron correlation parameters are to be introduced [18], namely the intra-atomic Hubbard repulsion energy U of two electrons of different spins in the same orbital state, U' of two electrons of different spins in the different orbital states and the lowest in energy Hund's doublon with two electrons of same spin in the different orbitals having energy $U' - J_H$, where J_H is Hund's rule coupling. Band hopping integral is concentration-dependent in consequence of taking into account the correlated hopping of electrons and two additional mechanisms of correlated hopping which are peculiar to doubly degenerated systems [18]. In distinction from the previously used models of electronic subsystem with orbital degeneracy, here we couple the electronic subsystem to the phonon one with strain-dependent hopping amplitude

$$t_{ij}(n, u) = t_{ij} \left(1 + \frac{BV_0}{2w} \bar{u} \right) \quad (2)$$

where $2w$ is the unperturbed band width ($w = z|t_k(n)|$), renormalized by correlated hopping processes [20], B is the characteristic constant for a particular compound and

V_0 is the unit cell volume. Electron-phonon interactions play an important role in dynamics of strongly correlated electron systems, as revealed by studies of Hubbard-Holstein model. The system energy is to be minimized with respect to lattice parameters, thus the lattice elastic energy is to be taken into account as well (the last term in Hamiltonian).

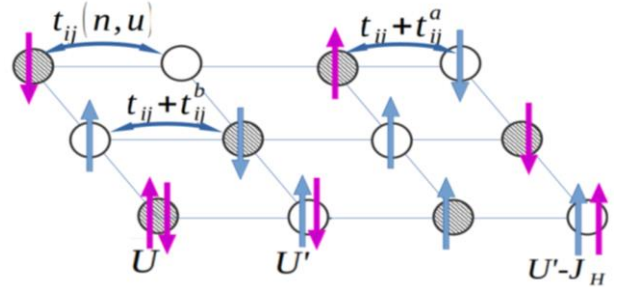


Fig. 1. Two-dimensional lattice of V atoms with possible electronic configurations of a site and different hopping amplitudes, dependent on the site occupation.

The averaged value of the lattice strain u is to be calculated in a self-consistent way from the minimum of the Gibbs thermodynamic potential

$$G = F + PV = F + NPV_0(1 + \bar{u}), \quad (3)$$

where F denotes free energy. From the relation $dF/du = -dH/du$, one has

$$\left\langle \frac{\partial H}{\partial u} \right\rangle + NpV_0 = 0. \quad (4)$$

Taking into account, that $\alpha u = \tau p V_0$, the equilibrium lattice strain is derived as

$$\bar{u} = -\frac{1}{V_0} \left(\frac{S}{N} \sum_{\bar{k}\gamma\sigma} \langle c_{\bar{k}\gamma\sigma}^+ c_{\bar{k}\sigma} \rangle + \frac{BV_0}{2w} \frac{1}{N} \sum_{\bar{k}\sigma} t_{\bar{k}} \langle c_{\bar{k}\gamma\sigma}^+ c_{\bar{k}\gamma\sigma} \rangle \right) - \frac{PV_0}{CV_0}, \quad (5)$$

where averages

$$\langle c_{\bar{k}\gamma\sigma}^+ c_{\bar{k}\gamma\sigma} \rangle = \int_{-\infty}^{\infty} dE J(E) = \sum_{\bar{k}} \int_{-\infty}^{\infty} dE J_{\bar{k}}(E) \quad (6)$$

are related to the single electron Green function spectral intensity $J(E)$. To study the strain-induced MIT we have to calculate Green functions and energy spectra for both paramagnetic metal (PM) state and antiferromagnetic insulator (AFI). Below, we restrict our consideration to the low-energy sector of the model, thus the higher-energy states of the lattice sites will be effectively excluded.

II. Results and discussion

2.1. Energy spectra for AFI and PM phases

For calculation of the single electron Green function we use the standard approach of equation of motion

$$E \langle \langle c_{p\gamma\uparrow}^+ \rangle \rangle = \frac{\delta_{pp'}}{2\pi} + \langle \langle c_{p'\uparrow}^+ \rangle \rangle \quad (7)$$

in which a variant of the projection method [20] is used to obtain a closed system of equation

$$[c_{p\gamma\uparrow}; \sum_{ij\gamma\sigma} t_{ij}^{ef} c_{i\gamma\sigma}^+ c_{i\gamma\sigma}] = \sum_l \varepsilon_{pl} c_{l\gamma\uparrow} + \sum_l \xi_{pr} c_{r\gamma\uparrow} \quad (8)$$

and the hopping terms are transformed in the mean-field ideology

$$t_{ij}^{ef} = t_{ij}(n, \bar{u}) + 2t_{ij}^a n_{\bar{\gamma}\sigma} + 2t_{ij}^b n_{\gamma\bar{\sigma}} \quad (9)$$

Here t_{ij}^{ef} is the effective concentration- and strain-dependent hopping amplitude introduced to enable the projection coefficients $\varepsilon_{pl}, \xi_{pr}$ calculation by the method of work [20]. The reason for applying the above projection procedure is the following. In V_2O_3 the transition from the high-temperature PM phase to the low-temperature AFI phase is accompanied by onset of alternating sublattices with opposite majority spin projections (their sites are shown as open or shaded circles in Fig. 1). The inverse transition can be induced by either the external pressure application or the chemical doping. Therefore, the physically distinct processes of electron hoppings from one of the two possible orbital states (shown as arrows of different colors in Fig. 1) to the corresponding orbital of the nearest neighboring site in a V_2O_3 film (with the opposite majority spin orientation) or to the next-nearest-neighbor (with the parallel majority spin orientation) are to be represented by different projection coefficients [21, 22]. To calculate the chemical potential we fix the electron concentration

$$\frac{1}{N} \sum_{i\gamma} (\langle c_{i\gamma\uparrow}^+ c_{i\gamma\uparrow} \rangle + \langle c_{i\gamma\downarrow}^+ c_{i\gamma\downarrow} \rangle) = n. \quad (10)$$

Finally, the quasiparticle energy spectrum below the transition temperature is

$$E_{1,2}^{\gamma\sigma} = -\mu + \frac{1}{2}(U' - J_H)n_{\bar{\gamma}\sigma} + \frac{1}{2}\varepsilon_{\bar{k}} + \frac{1}{2}\xi_{\bar{k}} \mp \frac{1}{2} \sqrt{\left((U' - J_H)n_{\gamma\sigma} + \varepsilon_{\bar{k}} + \xi_{\bar{k}} \right)^2 + 4\varepsilon_{\bar{k}}\xi_{\bar{k}}}. \quad (11)$$

When under an external action the energy gap closes, for the metallic paramagnet the band spectrum becomes

$$E^{\gamma\sigma} = -\mu + \frac{1}{2}(U' - J_H)n_{\bar{\gamma}\sigma} + t_{\bar{k}}^{ef}(n, \bar{u}). \quad (12)$$

In the metal-insulator transition point the energy spectrum, sublattice magnetizations, magnetic susceptibilities, conductivities all change, however in this study we just check the viability of the approach and investigate the conditions for the energy gap closure, leaving more detailed discussion for the forthcoming researches.

2.2. Lattice strain and the metal-insulator transition

Lattice contraction under the external pressure application or at chemical doping appears to be essential to switch the transition, which changes both the

conducting characteristics and the magnetic nature of the compound. For numerical calculation, the model rectangular electronic density of states has been used to speed up calculations, though more realistic DOS's are available for such quasi-two-dimensional systems. This restriction, however, does not undermine the soundness of our conclusions as the gap criterion is used to detect the transition point, which is quite insensitive to the DOS form [23].

Lattice strain u is found to depend weakly on the variation of the applied pressure and exponentially increase close to the transition point. Nevertheless, even a small variation of the lattice constant may trigger the transition and completely rebuild the single electron energy spectrum.

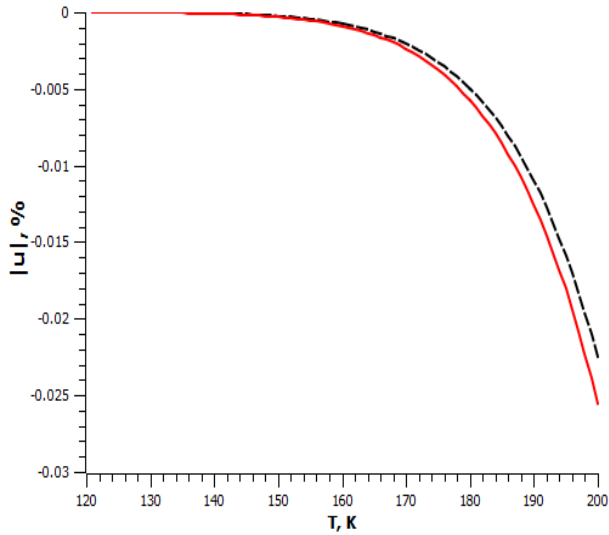


Fig. 2. Lattice strain as a function of the applied external pressure. The upper curve (dashed black one) corresponds to $pV_0/w=2$ and the lower one (shown by the solid red line) is built for $pV_0/w=2.1$.

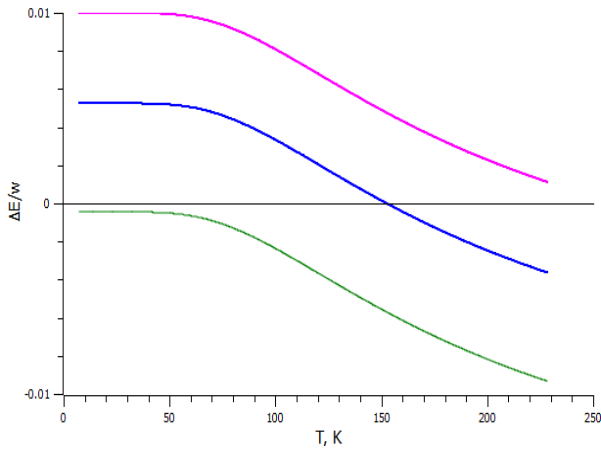


Fig. 3. The temperature dependences of the energy gap in the spectrum. The upper curve corresponds to $pV_0/w=2$, the middle one corresponds to $pV_0/w=2.05$ and the lower one – to $pV_0/w=2.1$.

The temperature dependences of the energy gap in the spectrum are shown in Figure 3 for close values of the external pressure. One can see that our approach allows us to reproduce three different regimes. The upper curve corresponds to the antiferromagnetic state with an energy gap; the middle one corresponds to the transition and the lower curve (with negative values which mean that no gap in the spectrum is present) corresponds to the metallic paramagnet state.

In Fig.5, the constructed phase diagram of the antiferromagnetic insulator (AFI) to the paramagnetic metal (PM) transition is shown, with wide boundaries of the transition region due to the uncertainty of the experimental findings for the model parameters we have used. For comparison, the experimental phase diagram of work [24] is given in Fig.4. One can see the qualitative agreement of PM/AFI phase boundaries on those diagrams.

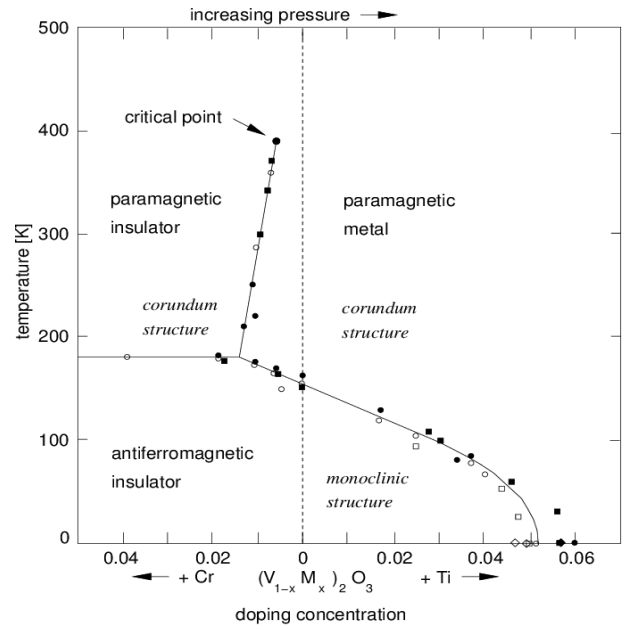


Fig. 4. Experimental phase diagram from work [24].

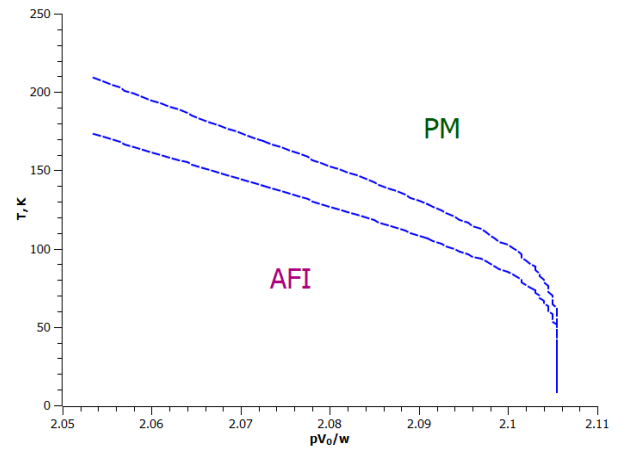


Fig. 5. AFI/PM phase boundaries calculated within the considered model.

Conclusions

In the doubly degenerated model of strongly correlated electron system the projection procedure allows to describe metal-insulator transitions as well as stabilization of magnetic orderings in the generalized Hubbard model (with electron-hole asymmetry). There is an important distinction of the present model from the non-degenerated one, namely, the lowest in energy doublon configuration is the Hund's spin triplet, which considerably reduces the energy benefit of having the alternate antiferromagnetic lattices if the hopping is intensified at increasing temperatures.

Our results support the findings of paper [18] which open new prospects for use of strain engineering to design novel electronic devices. The phase diagram allows the qualitative explanation of the transition, therefore the proposed model may serve as a basis for more detailed studies.

Skorenkyy Yuriy - Head of Physics Department at Ternopil Ivan Puluj National Technical University, 56 Ruska St, Ternopil, 46001, Ukraine;

Kramar Oleksandr - Associate professor of Physics Department, Ternopil Ivan Puluj National Technical University;

Dovhopyaty Yuriy – Lecturer of Physics Department, Ternopil Ivan Puluj National Technical University.

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Ю.Л. Скоренький, О.І. Крамар, Ю.М. Довгоп'ятій

Ефекти сильних електронних кореляцій в плівках оксидів ванадію

*Тернопільський національний технічний університет імені Івана Пулюя,
вул. Руська 56, м. Тернопіль, 46001 Україна, skorenkyy@mtu.edu.ua*

Досліджено перехід метал-діелектрик в двократно орбітально виродженій моделі квазідвовимірного матеріалу на основі плівки V_2O_5 , в якому ключову роль відіграє внутрішньоатомна кулонівська взаємодія та корельований перенос електронів, що зумовлює електрон-діркову асиметрію властивостей. З застосуванням процедури проєктування в методі функцій Гріна розраховано енергетичний спектр електронів, що дозволило змодельовати зміни властивостей матеріалу під дією зовнішніх впливів - тиску, легування та змін температури.

Отримані вирази для термодинамічного потенціалу та ширини енергетичної щілини дозволяють аналізувати можливі фазові переходи в системі, залежність її характеристик від зовнішніх впливів для цього класу матеріалів з сильними електронними кореляціями.

Ключові слова: перехід метал-діелектрик, сильні електронні кореляції, енергетичний спектр.