Pressure-temperature phase diagram of
generalized Hubbard model with
correlated hopping at half-filling

L. Didukh and V. Hankevych
Ternopil State Technical University, Department of Physics,
56 Rus’ka Str., UA–46001, Ternopil, Ukraine; E-mail: vaha@tu.edu.te.ua

In the present paper pressure-temperature phase diagram of a generalized Hubbard model with correlated hopping in a paramagnetic state at half-filling is determined by means of the generalized mean-field approximation in the Green function technique. The constructed phase diagram describes metal-to-insulator transition with increasing temperature, and insulator-to-metal transition under the action of external pressure. The phase diagram can explain paramagnetic region of the phase diagrams of some transition metal compounds.

Key words: phase diagram, metal-insulator transition, correlated hopping

PACS: 71.10.Fd, 71.30.+h, 71.27.+a

1. Introduction

In the recent few years a generalized Hubbard model with correlated hopping has been used widely to describe strongly correlated electron systems (see papers [1, 2] and references therein); the electron-hole asymmetry is a property of such a generalized Hubbard model as a result of the dependence of hopping integral on occupation of the sites involved in the hopping process. Recently, this model has been extended to the case of a doubly orbitally degenerate band [3].

The generalized Hubbard model has much richer properties than the well-known Hubbard model [4], and an usage of the electron-hole asymmetry conception allows to interpret the peculiarities of physical properties of narrow-band materials which are not explained by the Hubbard model. In particular, the experimentally observed electron-hole asymmetries of metal oxides conductivity, of cohesive energy of transition 3d-metals and of superconducting properties of high-temperature superconductors have been explained within the generalized Hubbard model with correlated hopping in papers [3, 4, 5], [6, 7], [8, 9, 10] respectively.

Despite the fact that phase diagram of generalized Hubbard model has been studied in works [11, 12, 13, 14, 15, 16, 17], researchers pay no attention to a determina-
tion of the model phase diagram in a paramagnetic state under the action of external influences, in particular pressure-temperature phase diagram. This task is related directly to the problem of metal-insulator transition description under the action of external pressure and temperature, namely the constructed pressure-temperature phase diagram of the model would allow to describe the observed metal-insulator transitions in narrow-band materials with changing of pressure and temperature. An interest to such transitions is caused by the theoretical point of view as well as the rich possibilities of its application (see, for example, monograph \[18\] and review \[19\]). Consequently, the goal of the present paper, being a continuation of previous work \[20\] where the temperature-induced metal-insulator transition was studied, is to determine the pressure-temperature phase diagram of generalized Hubbard model with correlated hopping in a paramagnetic state at half-filling. On basis of this phase diagram we describe metal-insulator transition under the action of external pressure and temperature.

2. Pressure-temperature phase diagram of the model

Taking into account an external hydrostatic pressure $p$ we write the model Hamiltonian in the following form \[5\] (in this connection see also Ref. \[21\]):

$$H = -\mu \sum_{i\sigma} a_{i\sigma}^{+} a_{i\sigma} + (1 + \alpha u)t \sum_{ij\sigma} a_{i\sigma}^{+} a_{j\sigma} + T_{2} \sum_{ij\sigma} (a_{i\sigma}^{+} a_{j\sigma} n_{i\sigma} + h.c.) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} NV_{0}\kappa u^{2},$$  \tag{2.1}

where $i, j$ are the nearest-neighbours sites, $\mu$ is the chemical potential, $a_{i\sigma}^{+}$, $(a_{i\sigma})$ is the creation (destruction) operator of an electron of spin $\sigma$ ($\sigma = \uparrow, \downarrow$) on $i$-site ($\bar{\sigma}$ denotes spin projection which is opposite to $\sigma$), $n_{i\sigma} = a_{i\sigma}^{+} a_{i\sigma}$ is the number operator of electrons of spin $\sigma$ on $i$-site, $U$ is the intra-atomic Coulomb repulsion, $t = t_{0} + T_{1}$, with $t_{0}$ being the matrix element of electron-ion interaction, $T_{1}$, $T_{2}$ are the correlated hopping integrals (matrix elements of electron-electron interaction), the primes at the sums in Hamiltonian (2.1) signify that $i \neq j$.

The latest term of the Hamiltonian has meaning of the elastic energy of a uniformly deformed crystal, where $\kappa$ is the “initial” (purely lattice) bulk elasticity, $N$ is the number of lattice sites, $u = \Delta V_{0}/V_{0}$ is the relative change of the volume in uniform strain ($V_{0}$ is the initial unit-cell volume). Formulating the Hamiltonian we have used the result of paper \[21\]: the dependence of a bandwidth $W$ on relative change of the volume $u$ in uniform strain can be written in the form $W = 2w(1 + \alpha u)$, where $w = z|t|$ ($z$ is the number of nearest neighbours to a site), $\alpha = \frac{\nu_{e}}{2w} \frac{\partial W}{\partial u} < 0$. We assume also that under the action of external pressure bandwidth changes only, and the matrix elements of electron-electron interaction (the correlated hopping integrals and intra-atomic Coulomb repulsion) do not depend on relative change of the volume.

As in papers \[2, 20\], using generalized mean-field approximation \[5, 22\] (an analog of the projection operation) in the Green function method we obtain for a
paramagnetic state at half-filling the energy gap width as

$$\Delta E = -(1 - 2d)(w + \tilde{w})(1 + \alpha u) + \frac{1}{2}(Q_1 + Q_2),$$  \hspace{1cm} (2.2)$$

$$Q_1 = \sqrt{[B(w - \tilde{w})(1 + \alpha u) - U]^2 + [4dz\ell'(1 + \alpha u)]^2},$$  \hspace{1cm} (2.3)$$

$$Q_2 = \sqrt{[B(w - \tilde{w})(1 + \alpha u) + U]^2 + [4dz\ell'(1 + \alpha u)]^2},$$  \hspace{1cm} (2.4)$$

where $B = 1 - 2d + 4d^2$, $d$ is the concentration of polar states (holes or doublons) which has been calculated in Refs. [2, 20]. $\tilde{w} = z|\tilde{\ell}|$, $\tilde{\ell} = t + 2T_2$, $t' = t + T_2$; $t$ and $\tilde{\ell}$ are the terms describing hopping of quasiparticles within the lower and upper Hubbard bands (hopping of holes and doublons) respectively, $t'$ describes a quasiparticle hopping between hole and doublon bands (the processes of paired creation and destruction of holes and doublons).

According to the method proposed for the s(d)-f model in paper [23], the equilibrium value of relative change of the volume $u$ is determined from the condition of minimum of the thermodynamic Gibbs’ potential

$$G = F + NpV_0(1 + u),$$  \hspace{1cm} (2.5)$$

where $F$ is the free energy. Using the known identity $\partial F/\partial u = \langle \partial H/\partial u \rangle$, Eq. (2.5) for the parameter $u$ can be represented as

$$\langle \frac{\partial H}{\partial u} \rangle + NpV_0 = 0,$$  \hspace{1cm} (2.6)$$

with $H$ being Hamiltonian (2.1). In the mean-field approximation passing to the space of quasi-momenta we get the following equation for relative change of the volume $u$:

$$\alpha u = \frac{2\alpha_1 V_0}{W N} \sum_{k\sigma} t_k \langle a_{k\sigma}^+ a_{k\sigma} \rangle + \tau p V_0,$$  \hspace{1cm} (2.7)$$

where $\alpha_1$ is the parameter which determines the quantity $\partial W/\partial V$, $2\alpha_1 V_0/W \approx 0.1$, $\tau \approx 0.05$ eV$^{-1}$ [21].

Taking into consideration the fact that within the generalized mean-field approximation the first term of right-hand side of Eq. (2.7) is equal to zero [24] at the point of metal-insulator transition, we obtain the relation between relative change of the volume $u$ and an external hydrostatic pressure $p$ as

$$\alpha u = \tau p V_0.$$  \hspace{1cm} (2.8)$$

Note that within the generalized Hartree-Fock approximation this equation is valid at the point of metal-insulator transition as well as in an insulating phase.

To determine pressure-temperature phase diagram of the model we use formula (2.2) for the energy gap width and the expression for concentration of polar states calculated in Ref [20]. Let us consider, for instance, the Mott-Hubbard compound NiS$_2$. This has two electrons half filling an $e_g$ band, the half-width of initial
(uncorrelated) band of this crystal is $w_0 = z|t_0| \approx 1.05$ eV [26, 27], and the initial unit-cell volume is $V_0 \approx 14.79 \times 10^{-30}$ m$^3$ [28]. It shows the transition from the state of a paramagnetic insulator to the paramagnetic metal state at a hydrostatic external pressure of 46 kbar and room temperatures. Thus the transition occurs for a decrease in volume of about 0.4% with no change in crystal structure [29, 30]. It also becomes metallic on alloying with Ni$_2$Se, and the behaviour of this system is discussed later in this section.

To calculate the model parameter $U$ we fix one of the points $(p = 22$ kbar, $T = 100$ K) of the experimental curve in the phase diagram (the dashed-line curve of figure [1]) and find the value of intra-atomic Coulomb repulsion $U$ at which the theoretical calculations within the present model reproduce this point. Thus, we obtain: $U_w = U_{w0} = 2.0168$ for the correlated hopping parameters $\tau_1 = T_1/|t_0| = 0$, $\tau_2 = T_2/|t_0| = 0$ (these values of $\tau_1$, $\tau_2$ correspond to the Hubbard model), $U_w = U_{w0}(1 - \tau_1) = 1.79107$ for $\tau_1 = \tau_2 = 0.1$, and $U_w = U_{w0} = 1.81437$ at $\tau_1 = 0$, $\tau_2 = 0.1$. Using these values of the model parameters we find the values of external hydrostatic pressure and temperature at which energy gap width is equal to zero (i.e. metal-insulator transition occurs).

The determined in this way pressure-temperature phase diagram of the model (figure [1]) describes metal-insulator transitions in a paramagnetic state under the action of external pressure and temperature in NiS$_2$, namely the constructed phase diagram describes metal-to-insulator transition with increasing temperature, and insulator-to-metal transition under the action of external pressure. Comparison of this theoretically determined phase diagram with the phase diagram of the compound NiS$_2$ shows a good agreement between the theory and experiment. Besides, the theoretical calculations within the model reproduce the experimental data of paper [29] which point out a presence of the energy gap width $\Delta E > 0$ in the ground state of NiS$_2$ and in absence of an external pressure.

![Figure 1](image-url)
also much better physics of the present model and the important role of correlated hopping.

Analogous phase diagrams can be constructed for the other compounds: \((V_{1-x}Cr_x)\)\(_2\)O\(_3\) \([18, 25]\), NiS\(_{2-x}\)Se\(_x\) \([26, 27]\) and \(Y_{1-x}Ca_x\)TiO\(_3\) \([31, 32]\) exhibiting such metal-insulator transitions. For example, the materials \((V_{0.96}Cr_{0.04})\)\(_2\)O\(_3\) shows a metal-insulator transition at a hydrostatic external pressure of 13 kbar and room temperatures; the transition occurs for a small decrease in volume of about 1\% with no change in crystal structure \([23]\). In \((V_{1-x}M_x)\)\(_2\)O\(_3\) (with \(M = Cr, Ti\)) the addition of Ti\(^{3+}\) ions to V\(_2\)O\(_3\) leads to insulator-to-metal transition, whereas the addition of Cr\(^{3+}\) ions results in metal-to-insulator transition. The simplest explanation is that the substitution of V\(^{3+}\) ion for Cr\(^{3+}\) ion leads to a band narrowing; the Cr\(^{3+}\) ion is a localized impurity and it deletes a state from the 3\(d\)-bands, deleting a state is equivalent to a band narrowing or an external pressure decreasing \([18]\) which drives the system towards the insulating phase. Likewise the addition of Ti\(^{3+}\) impurities is equivalent to an external pressure increasing.

In the Mott-Hubbard compound NiS\(_{2-x}\)Se\(_x\) electron hoppings between the sites of Ni occur by the chalcogenide sites (this is caused by peculiarities of the pyrite crystal structure \([33]\)), the substitution of S\(^2-\) ion for Se\(^2-\) ion in NiS\(_2\) leads to an increase of wave functions overlapping, consequently the probability of an electron hopping increases which is equivalent to a band broadening or an external pressure increasing. Therefore, the pressure-temperature phase diagram constructed for NiS\(_2\) can describe the experimental composition-temperature phase diagram \([26, 27]\) of the compound NiS\(_{2-x}\)Se\(_x\).

Note also that to construct phase diagram of the system \(Y_{0.61}Ca_{0.39}\)TiO\(_3\) we have to generalize the previous results obtained at half-filling to the case of a non half-filled band because this compound is characterized by such a band \([32]\).

In conclusion, in the present paper pressure-temperature phase diagram of the generalized Hubbard model with correlated hopping in a paramagnetic state at half-filling has been determined. The constructed phase diagram describes metal-to-insulator transition with increasing temperature, and insulator-to-metal transition under the action of external pressure. Comparison of this theoretically determined phase diagram with experimental data, in particular with the phase diagram of the compound NiS\(_2\) shows a good agreement between the theory and experiment. We have found that taking into account correlated hopping allows much better description of these experimental data than the Hubbard model; this testifies also much better physics of the present model and the important role of correlated hopping.

The determined pressure-temperature phase diagram of the model can explain paramagnetic region of the phase diagrams of the transition metal compounds: the systems NiS\(_{2-x}\)Se\(_x\) and \((V_{1-x}Cr_x)\)\(_2\)O\(_3\), calcium doped YTiO\(_3\).

References

1. Arrachea L., Aligia A. A. \(d_{x^2-y^2}\) superconductivity in a generalized Hubbard model. // Phys. Rev. B, 1999, vol. 59, No. 2, p. 1333–1338.
2. Didukh L. and Hankevych V. Metal-insulator transition in a generalized Hubbard model with correlated hopping at half-filling. // Phys. Stat. Sol. (B), 1999, vol. 211, No. 2, p. 703–712.
3. Didukh L., Skorenky Yu., Dovhopyaty Yu., and Hankevych V. Metal-insulator transition in a doubly orbitally degenerate model with correlated hopping. // Phys. Rev. B, 2000, vol. 61, No. 12, p. 7893–7908.
4. Hubbard J. Electron correlation in narrow energy bands. // Proc. Roy. Soc. A, 1963, vol. 276, No 1365, p. 238–257.
5. Didukh L. A modified form of the polar model of crystals. // Cond. Matt. Phys., 1998, vol. 1, No. 1(13), p. 125–144.
6. Didukh L. and Hankevych V. On correlation effects in a narrow-band model with electron-hole asymmetry // Low Temp. Phys., 1999, vol. 25, No. 5, p. 354–358.
7. Didukh L., Hankevych V., and Skorenky Yu. Some low-temperature properties of a generalized Hubbard model with correlated hopping. // Physica B, 2000, vol. 284-288, p. 1537–1538.
8. Hirsch J. E. Bond-charge repulsion and hole superconductivity. // Physica C, 1989, vol. 158, p. 326–336.
9. Hirsch J. E. Superconductivity and hydromagnetism. // Physica B, 1990, vol. 163, p. 291–298.
10. Hirsch J. E. Hole superconductivity from kinetic energy gain. // cond-mat/0005033, 2000, p. 1–4.
11. Aligia A. A., Arrachea L., and Gagliano E. R. Phase diagram of extended Hubbard model with correlated hopping at half filling. // Phys. Rev. B, 1995, vol. 51, No. 19, p. 13774–13777.
12. Arrachea L., Gagliano E. R., and Aligia A. A. Ground-state phase diagram of an extended Hubbard chain with correlated hopping at half-filling. // Phys. Rev. B, 1997, vol. 55, No. 2, p. 1173–1184.
13. Buzika B. Superconductivity in the Hubbard model with correlated hopping: slave-boson study. // Phys. Rev. B, 1998, vol. 57, No. 17, p. 10303–10306.
14. Strack R. and Vollhardt D. Hubbard model with nearest-neighbor and bond-charge interaction: exact ground-state solution in a wide range of parameters. // Phys. Rev. Lett., 1993, vol. 70, No. 17, p. 2637–2640.
15. Ovchinnikov A. A. Metal-insulator transition in the generalized Hubbard model. // J. Phys.: Condens. Matter, 1994, vol. 6, p. 11057–11069.
16. de Boer J., Schadschneider A. Exact ground states of generalized Hubbard models. // Phys. Rev. Lett., 1995, vol. 75, No. 23, p. 4298–4301.
17. Albverio S. and Fei S. -M. Some new exact ground states for generalized Hubbard models. // Europhys. Lett., 1998, vol. 41, No. 6, p. 665–670.
18. Mott N. F. Metal-insulator transitions. London, Taylor & Francis, 1990.
19. Imada M., Fujimori A., and Tokura Y. Metal-insulator transitions // Rev. Mod. Phys, 1998, vol. 70, No. 4, p. 1039–1264.
20. Didukh L., Hankevych V. Temperature-induced metal-insulator transition in a non-symmetric Hubbard model at half-filling // Condensed Matter Physics, 1999, vol. 2, No. 3 (19), p. 447–452.
21. Grigorchuk R. A, Stasyuk I. V. Electron-strained interaction and lattice contraction in crystals described by the Hubbard model. // Ukr. Fiz. Zh., 1980, vol. 25, No. 3, p. 404–410 (in Russian).
Pressure-temperature phase diagram of generalized Hubbard model...