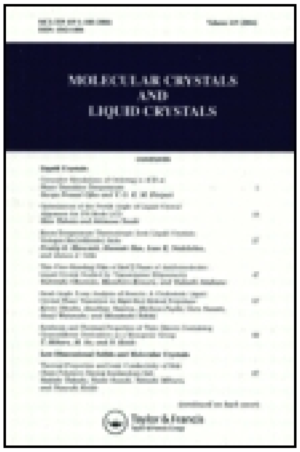

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Ferromagnetism of Fractal Hierarchy Dissipative Structures Based on Metalcontaining Heteroaromatic Systems

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FERROMAGNETISM OF FRACTAL HIERARCHY DISSIPATIVE STRUCTURES BASED ON METALCONTAINING HETEROAROMATIC SYSTEMS

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Abstract Fractal hierarchy dissipative structures (FHDS) can quite possibly manifest new non-phonon type of magnetic ordering. In this paper we formulate the principles of FHDS formation from microscopic to macroscopic levels, determine physico-chemical criteria for picking up a suitable heteroaromatic system as well as the type of metal to obtain fractal ferromagnetism. Conditions of fractal ferromagnetism existance can be deduced from the Stoner's criterion of ferromagnetism in Hubbard model applied to fractal geometry.

INTRODUCTION

Understanding of both successes and failures in creating non-metallic ferromagnets and high-T_c superconductors achieved recently has led to detailed studies of strongly correlated systems (SCS) prone to magnetic and superconducting ordering[1-5]. Both structure and composition of SCS (i.e. superconducting ceramics, metal-containing polyconjugated systems with strong bonds) can ease manifestation of interrelation between magnetic and superconducting ordering especially near the point of structural instability (metal-insulator transition) and antiferromagnetic transition leading to localized magnetic moments and incommesuarable spin waves[1,5-7]. This presentation is an endeavor to formulate some unified approach which would enable to:

- qualitatively explain numerous not yet understood experimental data on ferromagnetic bio- and polyconjugated polymers containing metal clusters;
- explain the mechanism responsible for formation of high-T_c ferromagnets based on metal-containing polyconjugated systems and understand the principles of

their creation starting from atomic (molecular) level to macroscopic organization of SCS amorphat.

FORMATION OF FHDS[10-12]

The fullest study on interconnection between crystal structure and its magnetic and conducting states is the Hubbard model[1,9]. The main parameters of this approach are the hopping energy of electron from one lattice site to other nearest site - $\hat{t}$, repulsive Coulomb energy between two electrons on the same site - $\hat{U}$, and a number of electrons with given spin s on i-nod - n_{is}. Conducting band width is normally chosen as a band parameter: $\hat{W}=2z\hat{t}$, where z is a number of nearest neighbors. For $\hat{U} \ll \hat{W}$ (Fermi fluid) and $\hat{U} \gg \hat{W}$ (SCS) cases the basis states are well defined which allowed to study the electric and magnetic behavior of the crystal depending on n_{is} in detail. The most interesting case of $\hat{U} \geq \hat{W}$, where an increase in n_{is} may lead to structural and compositional instability of the crystal due to impurity, electronic and magnetic phase separation[13,14], is especially difficult to handle, both analytically and numerically: the multiparticle basis state near the point of phase and kinetic transitions requires the renormalization of many physical quantities without any means to do so.

To clarify the situation in hand, one has to take into account important energetical, structural and kinetic pecularities of amorphous state, because the SCS in question are in fact structural glasses - compositionally and structurally non-equilibrium non-ergodic systems (amorphat) being far from thermodynamical equilibrium[12]. Amorphization of the crystal is often convenient to depict as a process of plastic deformation under different effects (e.g. high non-hydrostatic pressure P, acoustic, electric and magnetic fields, doping)[11,15]. Plastic deformation can be described by nucleation, multiplication and motion of structural and compositional defects in crystal lattice under external and internal mechanical stresses. The difference in topology and dimension of localization of translational (σ_{tr}) and rotational (σ_{rot}) components of the elastic stress tensor on micro-, meso- and macroscopic levels of deformation determines the types of elementary, mesoscopic and macroscopic defects whose sinergetic motion is actually the crystal amorphization. In multicomponent crystals besides structural defects there appear compositional ones which are disturbances in equilibrium stoichometry of distribution of the components by all sublattices at different levels of deformation.

The main process responsible for nucleation of elementary structural defect (ESD) is autolocalization of energy of structural excitation (E_{r0}) as a local change in the geometry of the basis lattice with heat losses (Q_{r0}) being minimal. Because of the quite small number of defects the amorphization of the crystal is accompanied by very non-uniform distribution of E_{r0} and Q_{r0} and loss of ergodicity: strong, long-range and anisotropic interatomic (intermolecular) interactions ($E_{in} \sim \hat{t}$) when $t_S \ll t_E$ (where $t_S \sim \hbar/\hat{t}, t_E \sim \hat{U}\hbar/\hat{W}^2$, z=1) lock defect lattice configurations inside local regions ($\xi_0 - \lambda_0$) due to high efficiency of rotational modes of tensor E_{in}, $\sigma_{rot} > \sigma_{tr}$. Since small displacements of atoms inside the ($\xi_0 - \lambda_0$) defect hinder the relaxation of elastic tensions, E_{r0} energy transforms into potential energy $U(r_0)$ by coherent reorganization of the crystal atoms over the characteristic length ξ_0, and by zeroing of the compensation elastic fields over the length λ_0. This scenario of the loss of ergodicity leads to the creation of a potential barrier Δ_{c0} around the ($\xi_0 - \lambda_0$) ESD on microscopical level of deformation - $n(\epsilon_0)$ and accompanied by the confinement and assymptotic freedom due to the dependence of the magnitude of the barrier Δ_{c0} on the number of displaced atoms and the distance between them[1,11]. Structural and compositional distortions and frustration of chemical bonds in ($\xi_0 - \lambda_0$) regions give birth to various aspects of amorphization, including the processes of impurity, electronic and magnetic phase separation[13,14]:

- mechano-physical because of the renormalization of $U(r_0)$, Δ_{c0}, t_S, t_E, shear modulus μ_0, longitudinal viscosity η_0, and diffusion coefficient D_0, density ρ_0, lengths ξ_0 and λ_0;
- thermodynamical owing to taking into account energy E_{r0}, heat Q_{r0}, enthropy $S(r_0)$ and temperature $\Theta(r_0)$ of reorganization: $E_{r0} \gg Q_{r0} \approx S(r_0)\Theta(r_0)$;
- electromagnetic due to deviation from basis distributions of electron ρ_e and spin ρ_s densities and related with them deviations in spectral characteristics of localized and delocalized phonon modes ρ_{ph};
- compositional and chemical due to deviations from stoichometry of the basis distribution of different chemical elements ρ_m.

This is the scenario of nucleation of elementary structural defect and microscopic level of deformation - $n(\epsilon_0)$, with their concentration being small, $\rho_{d0} \ll \rho_{dc}$, where ρ_{dc} is critical concentration (fig. 1).

Horizontal lines (fig. 1a) are related to a certain degree of resolution of energy spectrum $U(r)$ of ensembles of defects in physical space of basis crystal: for 11 types of ESD $U(r_0)$ has the best spatial resolution $\sim r_0$ on microscopic level - $n(\epsilon_0)$, with time resolution being of the order of $t_0 \gg t_S$; for 4 types of mesoscopic structural defects (mSD) formed by coherent merge of ensembles of ESD, $U(r_1)$ has worse spatial resolution $\sim r_1 \gg r_0$ on mesoscopic level of plastic deformation - $n(\epsilon_1)$ with time resolution $\sim t_1 \gg t_0$; for one type of macroscopic structural defect (MSD) formed by coherent merge of mSD ensembles, $U(r_2)$ has the worst spatial resolution $\sim r_2 \gg r_1 \gg r_0$ on macroscopic level of plastic deformation - $n(\epsilon_2)$ with time resolution $t_2 \gg t_1 \gg t_0$. Dark and light circles depict quasistationary states of ensembles of defects at different levels $n(\epsilon)$ with lifetimes $t(\epsilon)$. Hierarchy Cayley tree and ultrametric space (fig. 1b) are introduced for more adequate and easy-to-grasp description of the above-mentioned aspects of deformation and amorphization of the

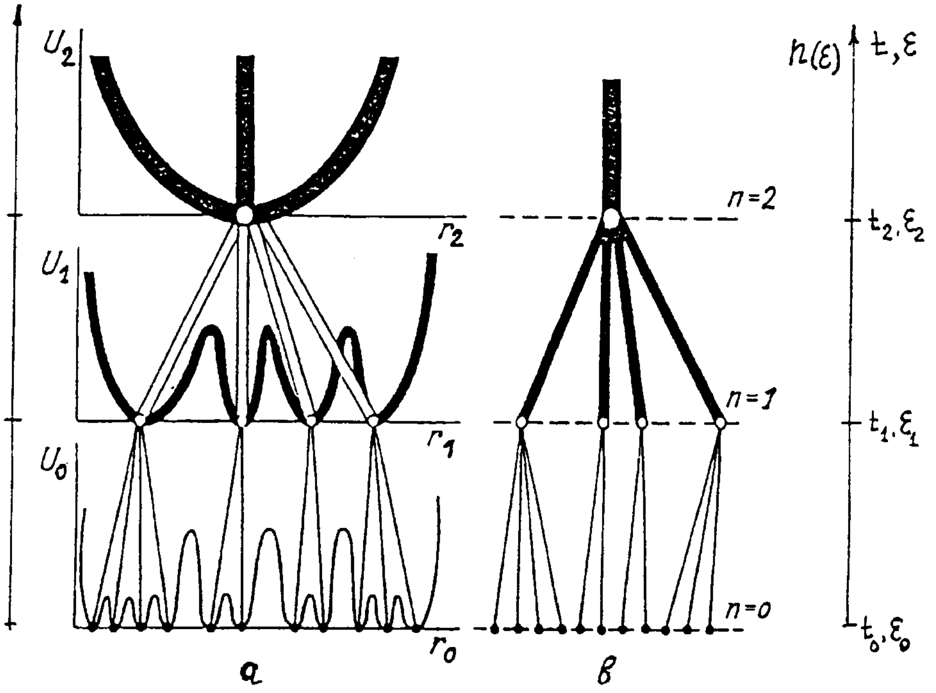

FIGURE 1. The shape of potential relief $U(r)$ of ensembles of defects in crystal on different structural levels of deformation $n(\epsilon)$ (a); and corresponding Cayley tree for 3 hierarchically interrelated $n(\epsilon)$-levels (b).

crystal with an increase of $n_{is}{\sim}n(\epsilon)$ as the processes of self-organization of hierarchy related ensembles of ESD, mSD and MSD during their sinergetic motion on $n(\epsilon(t))$-levels towards the top of Cayley tree. An interesting thing about such description of plastic deformation is that there are two types of averaging used: thermodynamical equilibrium inside individual ensembles for each type of ESD on $n(\epsilon_0(t))$-level is reached over time t_S, and then quasistationary equilibrium among ensembles of different types of ESD is attained over time t_0. Kinetic aspect of amorphization caused by weak recovery of ergodicity is determined by slow correlated merging of ESD into mSD over time $t_1 \gg t_0$, and mSD into MSD over time $t_2 \gg t_1$. Merging of ESD into mSD on $n(\epsilon_1)$-level and mSD into MSD on $n(\epsilon_2)$-level run as kinetic phase transitions (phase separation[13]) forming fractal hierarchy dissipative structure (FHDS) of the amorphat. Step-by-step recovery of ergodicity in the formation of FHDS-defects gives rise to fractal structure of the thermodynamical potential $\Phi\{U(\epsilon)\}$ in the configurational space of defects which largely affects dynamical, relaxation, electromagnetic, mechanical and thermodynamical properties of the SCS amorphat.

When degree of plastic deformation rises to $\epsilon_1 > \epsilon_0$ the height of $U(r_1)$ potential increases too because of arising correlations among ESDs during growth of their concentration $\rho_{d0}(\epsilon_1) \leq \rho_{dc}(\epsilon_0)$. $\kappa_0 = \lambda_0/\xi_0$ is a very important parameter of amorphization characterizing the ability of the crystal to accumulate a non-heat energy of excitation, with the enthropy production being minimal ($E_{r0} \gg S(r_0)\Theta(r_0)$, $E_{r0} > \Delta_{c0}$), by producing various types of ESD, establishing correlations among them, with ρ_{d0} increasing up to $\rho_{dc}(\kappa_0)$, which corresponds to the endurance limit of the crystal $\sigma(\kappa_0)$ on the $n(\epsilon_0)$-level. The number of hierarchy levels of plastic deformation $n(\epsilon)$ determined by the strength of the bond $\delta(\epsilon)$ among the defects of all levels is greater when E_{in} interactions decrease slower with increasing ϵ. If plastic deformation leads to the strengthening due to high efficiency of rotational modes $\sigma_{rot} > \sigma_{tr}$, then κ_0 and η_0 are large and the following hierarchy inequalities hold: $\kappa_0 \gg \kappa_1 \gg \kappa_2 \gg 1$ if $\lambda_1 = \lambda_0(1+\chi)^{-1}$ and $\xi_1 = \xi_0 w^{-1}$, where $\chi > 1$ and $w < 1$ are generalized susceptibilities to σ_{rot} and σ_{tr} modes on $n(\epsilon_0)$-level. In the opposite case ($\sigma_{tr} > \sigma_{rot}$) κ_0 and η_0 are small, there is no loss of ergodicity during plastic deformation, excitation energy quickly transforms into heat ($t_S \leq t_0$), and one observes the regime of viscous flow of softened crystal. Reaching $\rho_{dc}(\epsilon_0)$ leads to instability of the ESD lattice on $n(\epsilon_0)$-level because of appreciable correlations among defects, with the energy of their boundaries being large ($\Delta_c(\epsilon_0)$). That's why it is energetically favorable to create a more stable lattice of mSD (with concentration $\rho_{d1}(\epsilon_1)$) on $n(\epsilon_1)$-level, thus lowering the bottom of $U(\epsilon_1)$ potential and rising the height of $\Delta_c(\epsilon_1)$ barriers confining mSD. It should be noted that accumulation of ESD on $n(\epsilon_0)$-level takes place as the phase transition of the *II* kind, and coherent merge of $\rho_{dc}(\epsilon_0)$ into $\rho_{d1}(\epsilon_1)$ is the phase transition of the *I* kind. Because $U(\epsilon)$ and $\Delta_c(\epsilon)$ are rising functions, provided macroscopic continuity of the crystal on $n(\epsilon_2)$-level is intact ($\kappa(\epsilon_2) \gg 1$, $\rho(\epsilon_2) \ll \rho_{dc}(\kappa_0)$), kinetic transformations of ESD into mSD and the latter into MSD with increasing ϵ can happen only in strict order (fig. 1). The motion of ESD inside ($\xi_1 - \lambda_1$) region of mSD as well as the motion of mSD inside ($\xi_2 - \lambda_2$) region of MSD are determined by the energy $\Delta_c(\epsilon)$ at the boundaries and parameters of assymptotic freedom in the center ($Q_r \approx S(r)\Theta(r)$) on $n(\epsilon_1)$ and $n(\epsilon_2)$-levels, respectively. Such nature of the motion of defects under the effect of $U(\epsilon)$ potential separates degrees of freedom of defects as stochastic (hot) and mechanical (cold) ones[10]. Using the technique of generalized thermodynamical functions, one can determine the conditions of local quasiequilibrium and quasistationarity for ensembles of all types of defects on $n(\epsilon)$-levels of deformation (fig. 1) in order to adequately describe a complicated picture of chemical and phase transformations including impurity, electronic and magnetic phase separation, accompanying the amorphization of the crystal and the onset of inordinary mechanical, electrical, magnetic and thermodynamical properties (see the Table I). The evolution of structural instability on the $n(\epsilon_i)$-level ($\kappa(\epsilon_i) \leq 1$, $E_{ri} \geq Q_{ri}$, $\Delta_c(\epsilon_i) \leq Q_{ri}$) changes the mechanism of deformation from strengthening to deformational unhardening which qualitatively changes magnetic and electrical properties of the amorphized SCS crystal.

In order to relate structural and ferromagnetic and superconducting transitions in the Hubbard model to kinetic one in plastic deformation model[10], one needs to establish the trends of $\hat{U}$, $\hat{W}$, n_{is} with increasing $\rho_d(\epsilon)$. Since each $n(\epsilon)$-level is in correspondence with a certain $\rho_d(\epsilon)$ spectrum, then $\epsilon(t)$ growth leads to the following:

- if $\hat{U} \gg \hat{W}$ and E_{in} is strong and anisotropic ($\kappa_0 \gg \ln\kappa_0 \gg 1$. $\sigma_{rot} > \sigma_{tr}$), then the basis SCS lattice experiences the deformational strengthening accompanied by decreasing $\hat{U}$, and increasing $\hat{W}$, n_{is} and the number of hierarchy related levels $n(\epsilon)$ reflecting structural ($\rho_d(\epsilon)$), magnetic ($\rho_S(\epsilon)$), charge ($\rho_e(\epsilon)$)

and energy ($U(\epsilon)$), $\Delta_c(\epsilon)$, $Q_r(\epsilon)$) organization of the SCS amorphat. $\hat{U} \geq \hat{W}$ is attained near the point of the change in the regime of plastic deformation on $n(\epsilon)$-level if n_{is} is high enough which might result in ferromagnetic or superconducting ordering or both thanks to anisotropy of E_{in} and difference in parametres $\xi(\epsilon) - \lambda(\epsilon)$ for ferromagnetism and superconductivity[1]. If one looks at the Stoner-like criterion of ferromagnetism in the Hubbard model[9]

$$\frac{\hat{U} \cdot n_{is}}{\hat{W} - E_0} = 1 \tag{1}$$

one can see that long before reaching the macroscopic structural instability (formation of cracks, shear bands on the $n(\epsilon_2)$-level at $\rho_{dc}(\kappa_2)$) equation (1) holds, since for ferromagnetic (superconducting) ordering correlations among magnetic moments (carriers) are more important on $n(\epsilon_0)$ and $n(\epsilon_1)$-levels ($\epsilon_0 < \epsilon_1 < \epsilon_2$) than on $n(\epsilon_2)$ on which such correlations are destroyed. E_0 in (1) is the self-energy of one electron state;

If $\hat{W} \gg \hat{U}$ and E_{in} is strong and anisotropic ($\kappa_0 < 1$, $\sigma_{tr} > \sigma_{rot}$) basis lattice of Fermi fluid experiences the deformational unhardening accompanied by decreasing $\hat{W}$ and increasing $\hat{U}$, n_{is} and the number of $n(\epsilon)$-levels reflecting structural, magnetic, charge and energy organization of the frozen turbulent Fermi fluid. $\hat{U} \leq \hat{W}$ is attained near the point where the mechanism of deformation on the $n(\epsilon)$-level changes and n_{is} is large, which also may result in ferromagnetic or superconducting ordering.

However, these 2 cases do not represent the same type of ordering if $\hat{U}$, $\hat{W}$, and n_{is} assymptotically coincide because transitions from different basis lattices even under identical conditions of excitation would form different kinds of defects and their ultrametric spaces thanks to the loss of ergodicity and arising of hierarchy stochasticity. The above-mentioned allows us to understand the differences between these cases as well as those difficulties and failures of theoretical studies of ferromagnetism and superconductivity in SCS which hinder creation of high-T_c ferromagnets and superconductors based on SCS[1,9,10].

FHDS amorphat of SCS is formed via evolution of low-dimensional structures (cracks) which are fractal clusters of correlated displacements and turns of atoms on $n(\epsilon_0)$-level, ESD on $n(\epsilon_1)$-level etc. As a result the entire volume of the crystal

V_{cr} is self divided into hierarchy related volumes $V(\epsilon)$ on $n(\epsilon)$-levels whose position is uniquely determined by the defect correlation in respective $V(\epsilon)$ and considerable input from boundary energies $\Delta_c(\epsilon)$: only those structural elements can merge which are governed by sinergetic potential $U(\epsilon)$ over the distances $\sim \lambda(\epsilon)$ with displacements - turns $\sim \xi(\epsilon)$. Therefore, dynamic and relaxation processes as well as energy-mass-information transfers (chemical and physical transformations, ferromagnetic or superconducting ordering etc) occur only inside low-dimensional fractal clusters, since λ and ξ are much bigger than interatomic (intermolecular) distances. Fractal clusters are self-organized boundaries between $V(\epsilon)$ on $n(\epsilon)$-levels of plastic deformation, and various types of collective states including ferromagnetism and superconductivity can be achieved at these boundaries. These fractal clusters growing through V_{cr} form ultrametric space and Cayley tree of the self-division of V_{cr} into $V(\epsilon)$ on all $n(\epsilon)$-levels. This leads to 2 kinds of processes associated with the states inside $V(\epsilon)$ (hot degrees of freedom) and at their boundaries (cold degrees of freedom) which determine branching ratio j and similarity coefficient δ of the self-division of V_{cr}, respectively. Fractal dimension $D=\ln j/\ln\delta^{-1}$ shows the direction of self-organization of FHDS amorphat and $\Phi\{U(\epsilon)\}$. There are 3 possibilities:

1. $j\delta < 1$, $D < d_e$, $\kappa_0 \gg \ln\kappa_0 \gg 1$, $\sigma_{rot} > \sigma_{tr}$. Formation of amorphat stores the energy in fractal clusters and at the boundaries locking the energy of excitation inside fractal clusters $(\Delta_c(\epsilon))$, d_e - dimension of self-organization in physical space, $d_e=1$.
2. $j\delta > 1$, $D > d_e$, $\kappa_0 \leq 1$, $\sigma_{tr} > \sigma_{rot}$. Self-decay of FHDS amorphat takes place at the expense of freeding previously stored energy in fractal clusters and at their boundaries.
3. $j\delta=1$, $D=d_e=1$. Quasiequilibrium structural transitions between various ordered phases in quasiergodic amorphat occur.

Hence, j, δ, D, and $n(\epsilon)$ carry a very important physical information about amorphization processes: inequality $D \neq d_e$ points to the fact that physical and chemical processes responsible for formation of the amorphat are in fact non-equilibrium non-uniform processes of self-organization (self-decay) of non-ergodic systems whose collective properties can be assessed using j and δ, and $n(\epsilon)$ can be used to estimate E_{in}-interactions. It's clear that parameters of Cayley tree in the ultrametric space are connected with the history of formation of the structural and energetical levels of the amorphat (structural and compositional memory). It's worth noting that

SCS amorphat has also dynamical memory which is a measure of time-reversibility of the processes in hand. Specific diffusion and wave equations of energy and mass transfer, relaxation equations in FHDS employ fractional differential and integration operators whose indices of power are quantitative measure of structural and dynamical memory. Such fractal hierarchical kinetics describes the formation dynamics of fractal clusters, the processes of impurity, electronic and magnetic phase separation which initiate the superconducting/ferromagnetic ordering[5–7,13,14].

The most important things for FHDS-based ferromagnets and superconductors are their time stability and value of T_c. As for T_c, its value might be considered to be such temperature T_f under which fractal clusters - defects formed over time $t_m(\epsilon_0)$ preserve their maximum hierarchical memory on all levels $n(\epsilon_c)$ of deformation in time $t_M(\epsilon_c)$ - time of coherent decay of FHDS amorphat:

$$t_m(\epsilon_0, \Delta_{c0}) \propto n(\epsilon_c)\tau_0 \exp\{U(\epsilon_0, \Delta_{c0})/\Theta(\epsilon_0)\} \tag{2}$$

$$t_M(\epsilon_c, \Delta_c(\epsilon_c)) \propto \tau_0 \exp\{U(\epsilon_c, \Delta_c(\epsilon_c))/Q_r(\epsilon_c, \kappa(\epsilon_c))\} \tag{3}$$

where $U(\epsilon_0, \Delta_{c0})$ is the minimal height of potential barrier on microscopic level $n(\epsilon_0)$, τ_0 - time of attaining of thermodynamical equilibrium in ESD ensembles, $\Theta(\epsilon_0)$ is a structural temperature of $n(\epsilon_0)$-level close to T_{ext}, $U_c(\epsilon_c, \Delta_c(\epsilon_c))$ is the maximum height of the potential barrier on $n(\epsilon_c)$-level where the critical concentration of all defects $\rho_{dc}(\kappa_c)$ and endurance limit $\sigma_c(\kappa_c)$ are attained, $Q_r(\epsilon_c, \kappa(\epsilon_c))$ is the total heat losses on all hierarchically related levels $n(\epsilon_c)$. If one analyzes (2) and (3) taking into consideration mechanisms responsible for increase in barriers $U(\epsilon)$ heights and weakening of hierarchical bond $\delta(\epsilon)$ among defects on $n(\epsilon)$-levels with increasing ϵ, one would see that t_m increases, and t_M decreases if $\delta(\epsilon)$ diminishes[11]. Such behavior of t_m and t_M is related to weakening anisotropy and decreasing range of E_{in} interactions as well as increasing heat losses $Q_r(\epsilon, \kappa)$ due to adiabatic self-heating of $(\xi - \lambda)$ defect regions. This leads to their optimized concentration $\rho_d^0(\epsilon^0)$ on the $n(\epsilon^0)$-level where t_m and t_M equalize. Hence, one can obtain a qualitative criterion of high T_c if $t_m \ll t_M$ and optimized $\rho_d^0(\epsilon)$ on the $n^0(\epsilon)$-level:

$$T_f = T_c(\rho_d^0(\epsilon), n^0(\epsilon)) \leq \frac{U(\epsilon)\Theta(\epsilon_0)}{U(\epsilon_0)\ln(n^0(\epsilon)t_M/t_m)} \tag{4}$$

TABLE I. Conditions of quasiequilibrium and quasistationarity of FHDS

A

$$[\mu_{kl}\bar{n}_k\bar{n}_l]_{i,m} = [(\bar{u} - \theta \cdot S)\delta_{kl} + \hat{\sigma}_{kl}\Omega_a + \Delta_c + X_e \cdot x_e]_{i,m}$$

$$[\mu_{kl}\bar{n}_k\bar{n}_l]_{i,m} = [\mu_{kl}\bar{n}_k\bar{n}_l]_{i,m+1} \qquad k, l = \{x, y, z\}$$

$$[\nu\mu_{kl}\bar{n}_k\bar{n}_l]_{i,m} = [\nu\mu_{kl}\bar{n}_k\bar{n}_l]_{i,m+1} \qquad i = 1, 2, ..., j \quad m = 1, 2, ..., n(\epsilon)$$

$$[\bar{\sigma}_{kl}\bar{n}_k\bar{n}_l - \frac{\Delta_c}{\Omega_d} - \frac{X_e \cdot x_e}{\Omega_e}]_{i,m} = -P_{ext}\{X_e\}$$

$$\Theta_{i,m} = T_{ext}, \qquad \Delta_{c,im} < T_{ext} \qquad \eta_m > D_m^{-1}$$

$$\Theta_{i,m} = 0, \qquad \Delta_{c,im} > T_{ext}$$

B

$$\mu_{i,1} < \mu_{i,2} < ... < \mu_{i,m} \qquad \Delta_{c,i1} < \Delta_{c,i2} < ... < \Delta_{c,im}$$

$$u_1 < u_2 < ... < u_m, \qquad u_1 > \frac{P\Omega_{d1}}{\kappa_1}, \quad u_m \geq \frac{P\Omega_{dm}}{\kappa_m}$$

$$\nabla u_1 > \nabla u_2 > ... > \nabla u_m, \qquad \nabla u_1 > \frac{u_1}{\lambda_1}, \quad \nabla u_m \geq \frac{u_m}{\lambda_m}$$

$$(\frac{\hat{\sigma}\Omega_a}{\theta S})_{i1} > (\frac{\hat{\sigma}\Omega_a}{\theta S})_{i2} > ... > (\frac{\hat{\sigma}\Omega_a}{\theta S})_{im} \qquad \kappa_1 \gg \kappa_2 \gg ... \gg \kappa_m > 1$$

Part **A** of the table represents conditions of thermodynamical, phase, chemical and mechanical equilibria, and part **B** - conditions of the quasistationarity of FHDS. μ, $\bar{u}$, θ, and S are specific chemical potential, internal energy, temperature and enthropy, respectively. $\Omega_a, \Omega_d, \Omega_e$ are unit volumes of atom, defect and charge, respectively. T_{ext}, P_{ext} are external temperature and pressure, $X_e(\mathrm{H}_e,\mathrm{E}_e)$, $x_e(\mathrm{p}_e, \mathrm{M}_s)$ are generalized forces and coordinates, p_e and M_s are electric polarazability and magnetization, respectively, E_e and H_e are electrical and magnetic fields. $\bar{n}_k$, $\bar{n}_l$ are unit normal vectors at the boundary of fractal cluster, ν_{im} are stoichometrical coefficients in i-channel on m-level, η_m, D_m^{-1} are viscosity and diffusion coefficient on m-level.

In our case of metal-containing polyconjugated polymers T_f can be assessed by comparison to T_c of spin and structural glasses[1,11]: $T_0 < T_f \leq 0.5T_m$, where T_0 is the temperature at which ESDs on $n(\epsilon_0)$-level become unstable (small $\rho_{d0}(\epsilon_0)$) due to fast recovery of ergodicity: $t_R \ll t_m$, $T_0 < U(\epsilon_0)$ and $\Theta(\epsilon_0) \rightarrow T_{ext}$, t_m is finite; T_m is the melting temperature of basis lattice. Thus, one can estimate the range in which T_c for metal-containing polyconjugated systems lies: $l \times 10\mathrm{K} < T_c \leq m \times 100\mathrm{K}$, where $l \approx$ 5-10, $m \approx$ 2-4 if $t_M \sim 10^7$-10^8 sec (t_m is hard to estimate because it depends on $\delta(\epsilon)$ and $n(\epsilon)$)[3-7].

Qualitative analysis of equation (2)-(4) and conditions from the Table I can give us some ideas how to raise T_c and t_M, and lower t_m:

1. Lowering the amount of heat loss on all levels of amorphization of the basis lattice. To attain this one need to get rid of all sources of enthropy in the formation of fractal hierarchy clusters of defects. One can form FHDS - defects at low temperatures T_s ($T_c < T_s < 0.5T_m$) using mechanical (acoustic), electrical and magnetic fields, with their energy, frequency and spatial parameters determining the types of defects and the strength of their hierarchical conjugation $\delta(\epsilon)$ as well as the structure of potential barriers $(U(\epsilon), \Delta_c(\epsilon), Q_r(\epsilon))$, direction and rate of the processes of the impurity, electronic and magnetic phase separation, as a source of the initiation of chemical and physical transformations of the basis lattice. It is this multifractal hierarchical excitation that ought to predominantly form stable FHDS of those defects whose sinergetic dynamics on $n(\epsilon)$-levels result in desired type of ordering: ferromagnetic or superconducting.

2. The choice of composition and structure of basis lattice of metal-containing polyconjugated systems. Part A of the Table I gives us a tool to pick heteroaromatic (C,N,O elements) π-conjugated systems from all other π-conjugated systems as the most promising systems suitable to obtain high-T_c ferromagnets/superconductors based on metal-containing π-conjugated polymers. Part B of the Table I tells us that it's better to use soluble olygomers consisting of 2-3 monomers of metal-containing heteroaromatic conjugated systems[5,17] to form the lattice. Polymerization of such olygomers by above-mentioned field methods with minimal heat losses leads to the formation of FHDS amorphat in hierarchically conjugated physical and chemical transformations (fig.1). Concentration and type of metal in olygomers as well as the parameters of the multifractal fields[5,6] are chosen in such a way that to obtain ferromagnetic or superconducting ordering. In case of ferromagnetism, Fe and/or Co-containing olygomers are utilized, with metal concentrations not exceeding 1-2%, so that to predominantly form metal nanoclusters (10-20 Å)[6]. For superconductivity it's better to use metals which are found in high-T_c ceramics (Y, Tl, Eu)[5,16], and

avoid using metals prone to forming localized magnetic states. The concentration of metal dopants should be less than in case of ferromagnetism[5-7].

FERROMAGNETIC ORDERING IN FHDS AND THE PROBLEM OF FERROMAGNETIC CONTAMINATION

Almost 40 years of study on magnetic properties of biopolymers and polyconjugated systems proved the interrelation between their ferromagnetism and structure [2,5,8,17]. It's widely considered that in all cases ferromagnetic behavior is observed owing to ferromagnetic impurities because high-T_c and low saturation magnetization M_s in low magnetic fields H_s are characteristic of them. However, in some carefully performed experiments the concentration of metal (Fe, Co) wasn't high enough, even if all the metal was considered to be in the form of ferromagnetic domains, to account for all magnetization. In addition, in this approach it would be impossible to explain how non-uniform metal-polymer structure forms, whereas the our approach can easily account for this phenomenon. Non-heat excitation of the non-magnetic basis SCS (biopolymers[8] and polymers with heteroatoms in π-conjugation chain[2,17] containing small quantities of bound iron atoms) at the expense of the energy of chemical and physical transformations helps to form low-dimensional fractal clusters of defects whose $\Phi\{U(\epsilon)\}$ potential governs the kinetics of the processes of impurity, electronic and magnetic phase separation and the formation of polymer matrix "coated" nanoclusters of iron (10 - 20 $\AA$). According to the conditions of the self-organization of FHDS (fig.1, Table I, (2)-(4)) ferromagnetic ordering occurs under the sinergetic part of $V(\epsilon)$ potential - $\Phi\{U(\epsilon)\}$ which governs the processes of collective impurity and electronic phase separation and provides the high density of magnetic atoms in fractal clusters. The magnitude of potential barriers $U(\epsilon), V(\epsilon)\Delta_c(\epsilon)$ for SCS in hand[2,5,6,8,17] is few tenth of eV (0.1 eV - 1 eV) which determines the "coating" of iron nanoclusters in polymer "dress" (strong binding of electron states between iron atoms and polymer molecules in fractal clusters). This results in strong exchange interactions between magnetic moments of iron atoms as inside clusters as between clusters via mobile strongly spin-polariz π-electrons since the energy of a ferromagnetically "coated" cluster turns out to be lower than the energy of the non-magnetic basis lattice[13]. All necessary conditions (1) - (4) can be already fulfilled on the mesoscopic $n(\epsilon_1)$-level of the self-organization of the FHDS amorphat. The instablity of non-equilibrium non-ergodic SCS to the exposure to external effects (heat, moisture, oxygen and electron acceptors and donors) leads with time to the destruction of strong correlations between magnetic moments of iron clusters (decreasing $t_M, \delta(\epsilon)$, recovery of ergodicity of the FHDS amorphat).

The presented concept not only explains the differences and pecularities in ferromagnetic properties of metal-containing π-conjugated systems[2-8,16,17], but also allows to distinguishly form stable high-T_c non-linear active media with various properties (ferromagnetic, superconducting, non-linear optical etc.) by governing the fractal chaos. The authors believe research in molecular electronics based on heteroaromatic π-conjugated systems self-organized into multifractal hierarchical dissipative structures to be promising.

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REFERENCES

1. Yu.A. Izyumov, M.I. Katsnel'son, Yu.N. Skryabin, Magnetism of Collective Electrons, (Fiz-Mat Literatura, Moscow, 1994).
2. A.L. Buchachenko, Chem.Usp, 59, No. 4, 529 (1990).
3. A.F. Hebard, Physics Today, 11, 26 (1992).
4. P.M. Allemand, K.C. Khemani, A. Koch et al, Science, 253, 311 (1991).
5. M.L. Lyubchenko, L.S. Lyubchenko et al, Polymer Yearbook, 14 (1997).
6. M.L. Lyubchenko, L.S. Lyubchenko et al, Mol.Cryst.Liq.Cryst, 274, 205 (1995).
7. L.S. Lyubchenko, S.V. Stepanov, M.L. Lyubchenko et al Phys.Lett.A, 162, 69 (1992).
8. L.A. Blumenfeld, Sov.Phys.Dokl., 148, 361 (1963).
9. R.R. Nigmatullin, Abstracts of the 27-th Congress AMPERE, 1, 354 (1994).
10. A.I. Olemskoi and A.Ya. Flat, Phys.Usp, 36, 1087 (1993).
11. A.I. Olemskoi, I.A. Sklyar, Phys.Usp, 162, 29 (1992).
12. A.I. Olemskoi, E.A. Toropov, Fiz.Met.Mater., 7, 5 (1991).
13. E.L. Nagaev, Phys.Usp, 165, 529 (1995).
14. V.S. Dotsenko, Phys.Usp, 165, 481 (1995).
15. V.E. Panin, Structural Levels of Plastic Deformation and Destruction, (Nauka, Novosibirsk, 1990).
16. V.I. Il'ychev, M.A. Savchenko, A.V. Stefanovich, High-T_c Superconductivity of Ceramic Systems, (Nauka, Moscow, 1992).
17. B.G. Antipov, S.V. Kryuchkov et al, Coord. Chem., 21, 716 (1995).