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Charge transfer excitons in HTSC cuprates and nickelates

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An analysis of the optical properties of compounds based on 3*d*-elements provides valuable information about the electronic structure of the ground state and low-energy excitations. Thus, we show that the analysis of charge-transfer $d-d$ excitons in the dielectric antiferromagnetic phase of cuprates and metastable low-energy electron-hole EH dimers being a result of their evolution after electron-lattice relaxation, turns out to be very fruitful not only for describing linear and nonlinear optical properties and photoinduced effects, but also to develop a promising model of charge triplets to describe the low-energy electronic structure and $T-x$ phase diagrams of active CuO_2 planes in cuprates of the T-La_2CuO_4 or T'-Nd_2CuO_4 type, as well as NiO_2-planes in nickelates of the $RNiO_2$ type, and their evolution with changes in the main energy parameters.

Keywords: cuprates, nickelates, charge-transfer excitons, electron-hole dimers, charge triplets.

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1. Introduction

With the opening in early 1986 high-temperature superconductivity (HTSC) in doped cuprates based on La_2CuO_4 [1] there is a sharp increase in interest in the theoretical and experimental study of a wide class of quasi-two-dimensional cuprates and other strongly correlated magnetic systems based on 3*d*-, 4*d*- and 5*d*-metals with anomalous behavior of the charge subsystem. Actually, it was since then that the term „strongly correlated systems" began to denote a new direction in the physics of condensed matter and magnetism, the term „novel magnetism" appeared. Over the past thirty-five years, not only the class of HTSC cuprates has been significantly expanded and „topped" with mercury cuprate $HgBa_2CaCu_2O_{6+x}$ with a critical temperature of 133 K, but it was also discovered quite a few new compounds based on transition elements with unique physical properties that have become the focus of the research community. Among them there are new superconductors, such as strontium ruthenate Sr_2RuO_4, possibly the first solid-state spin-triplet superconductor, 2D nickelates based on $RNiO_2$, which are isoelectronic and isostructural to cuprates, as well as a large class of iron-based superconductors (ferropnictides FePn and ferrochalcogenides FeCh), systems with colossal magnetoresistance such as manganites based on $LaMnO_3$, systems with unusual metal-insulator transitions such as 3D nickelates $RNiO_3$, ferrates $AFeO_3$ (A = Ca, Sr, Ba). In reality, all these „new" systems are strongly correlated with respect to typical weakly correlated systems such as simple metals, but in terms of the magnitude of local correlations they are obviously inferior to the large family of „old" spin-magnetic systems based on transition metals such as oxides of Mn, Cr, Fe, Co, Ni, various ferrites, which are usually weakly anisotropic spin magnetic insulators. It is this „intermediate" position that determines the unique properties of the new systems, indicating a strong competition between the spin, orbital, charge, and lattice degrees of freedom. In particular, all these systems exhibit instability to charge transfer, disproportionation, and mixed valence accompanied by strong lattice fluctuations. Today, there is no consensus on a theoretical model that allows to describe the diversity of static and dynamic phase states of new systems on equal footing.

In this paper, we show how an analysis of optical properties, primarily charge transfer (CT) transitions, can make, if not a decisive, then a fundamentally important contribution to clarification of the nature of unusual properties of new strongly correlated compounds based on 3*d* metals. The article discusses the role of *d*-*d*-type CT excitons and electron-hole (EH) dimers as a result of exciton relaxation in the formation of exotic normal and HTSC states for „old" quasi-2D-cuprates and „new" quasi-2D nickelates. In Section 2 some features of the crystal and electronic structures of cuprates and nickelates are briefly considered and it is concluded that it is possible to describe them within a single scenario. Section 3 is devoted to *d*-*d*-CT-excitons in the insulating antiferromagnetic phase of „parent" cuprates/nickelates and their evolution on the example of cuprates. Lots of attention is paid to the manifestation of excitons and EH dimers in various optical effects. Section 4 shows the role of EH dimers in the formation of unusual phase states of both parent and doped cuprates/nickelates, as well as in the development of a

promising model of charge triplets; the effective Hamiltonian and typical phase diagrams of the CuO_2/NiO_2 planes are presented. A brief conclusion is presented in Section 5.

2. Quasi-two-dimensional cuprates and nickelates with ionic configuration $3d^9$

The recent discovery of superconductivity in quasi-two-dimensional rare-earth nickelates $RNiO_2$ (R=Nd, Pr, La) with hole doping [2–5] (see also review papers [6–8]) posed a new challenge for „superconducting" community. These nickelates are intriguing analogs of HTSC cuprates due to the formally identical $3d^9$ electronic configurations of the $3d$ ions and the similar crystal structure of the NiO_2 and CuO_2 planes, which would seem to allow considering quasi-2D cuprates and nickelates on equal footing. First of all, this should apply to cuprates with an ideal T' structure, in which CuO_4 clusters, like NiO_4 in nickelates, do not have apex oxygen ions. However, in real bulk samples of T' cuprates, for example, Nd_2CuO_4, it is difficult to get rid of a low concentration „of parasitic" apex oxygen. The maximum closeness to the ideal T' structure can only be achieved in thin films of Nd_2CuO_4 [9], the properties of which surprisingly differ fundamentally from bulk samples. Thus, while bulk samples of the parent Nd_2CuO_4 are characterized by the antiferromagnetic insulating (AFMI) ground state, thin films of Nd_2CuO_4 are superconductors with a critical temperature of approximately 30 K and a complete absence of signs of magnetic order [9]. A similar situation is also observed in quasi-2D nickelates, where superconductivity is found only in thin films, while bulk samples are rather insulators without long-range magnetic order [10]. As in T'-cuprates, this is due to „parasitic" apex oxygen atoms, the complete elimination of which is hardly possible with „topotactyl" method for obtaining samples of quasi-2D nickelates [6–8,10]. These surprising effects of a radical change in properties during the transition „thin film - bulk sample" in cuprates and nickelates with T'-structure testifies not only to the important role of even a small fraction „of defective" apex oxygen, but also directly indicates the proximity of the free energies of the insulating and superconducting phases and the instability of cuprates and nickelates with respect to charge fluctuations. Moreover, the history of superconductivity in apexless cuprates and nickelates with T' structure, including the discovery of superconductivity in nominally undoped systems Nd_2CuO_4 [9] and $LaNiO_2$ [4], forces us to reconsider the very concept of the „parent" compound, which is still most often associated with an undoped stoichiometric composition with the ground antiferromagnetic insulating AFMI state, typical only for cuprates with an T structure.

Below „parent", we mean cuprate or nickelate with hole half-filling of in-plane centers CuO_4 (NiO_4), which, depending on the parameters of local and non-local correlations, transfer and exchange integrals, as well as „external" crystal field generated by the out-of-plane environment can have a different ground state from antiferromagnetic insulator (AFMI), unusual Bose superconductor (BS), Fermi metal (FL) to non-magnetic charge-ordered (CO) insulator [11–16]. Obviously, these phases will differ not only in electronic but also in lattice degrees of freedom, the interaction of which ensures the minimum of the total free energy. In addition, the competition of several possible phases with similar energies will lead to phase separation, which will have a significant effect on the observed physical properties.

Curiously enough, the absence of long-range magnetic order in quasi-2D nickelates is still considered as an indication of the mechanism of superconductivity, which is different from that of cuprates. In this connection, the idea of the specific role of the $5d$-shells of La, Nd, Pr ions has appeared and is being widely discussed, based mainly on the ambiguous results of theoretical calculations [6–8,17], but has not received convincing experimental confirmation in practically the only paper [18] on the interpretation of XAS (X-ray absorption spectroscopy) and RIXS (resonant inelastic X-ray scattering) spectra. At present, the question of the role of the $5d$ orbitals of the R-ion remains debatable [8]. A number of authors (see [17], as well as review articles [7,8] and references therein), referring to the simplified classification of Zaanen–Sawatsky–Allen insulators (ZSA, [19]) point to the „parent" nickelates tendency towards Mott-Hubbard (MH) insulating ordering, in contrast to the „parent" cuprates, considered as charge-transfer (CT) insulators. However, the ZSA classification [19] operates on „ill-defined" atomic $2p$- and $3d$-states with „ill-defined" values U and Δ_{pd}. A more adequate classification should be based either on the cluster approach [20], or on direct experimental data on the nature of the fundamental absorption band or optical charge transfer gap: for CT insulators, it is associated with p-d transitions, in fact localized within clusters of the CuO_4 or NiO_4 type, while for MH insulators it is associated with the so-called d-d charge transfer transitions localized minimum on a pair of neighboring clusters. In this sense, the parent T cuprates are MH insulators (see below).

Thus, in our opinion, there are no fundamental qualitative differences in the electronic structure of nickelates and cuprates, primarily cuprates with an T' structure. The unusual properties of cuprates and nickelates are the result of the „competition" of various parameters that govern the ground state of the CuO_2/NiO_2. Thus, if for the overwhelming majority of parent cuprates there is an antiferromagnetic insulating phase, which corresponds to the limit of strong local correlations, then this phase was not found in the parent nickelates $RNiO_2$, which can be associated with a lower value or even a change in the sign of the parameter of local correlations. Nevertheless, we show below that the nonmagnetic phases of nickelates, as well as those of cuprates, can be considered as the result of the evolution of some, albeit hypothetical, AFMI phase.

3. *d-d* charge-transfer excitons and their evolution in parent AFMI cuprates

Cluster models have proven to be reliable working methods for strongly correlated transition and rare earth metal compounds. They have a long and well-deserved history of applications in optical and electronic spectroscopy, magnetism and magnetic resonance. It is cluster models that allow, from a unified standpoint, to give an adequate description of various allowed and forbidden optical transitions in the insulating phase of strongly correlated systems based on *d*-elements.

The cluster model, which is a generalization and improvement of the crystal field and ligand field models, provides a physically clear picture of the complex electronic structure and energy spectrum, as well as the opportunity of numerical simulation. Unlike the popular, but primitive „atomic" approach, which operates with configurations like d^9, d^9L, d^9L^2, where L is a hole on the oxygen ligand, the cluster approach, taking into account the correct local symmetry and *p-d*-covalence, allows to give an adequate description of many-electron configurations of clusters, and hence of correlation effects, electron-vibrational interaction, and relatively weak interactions, such as spin-orbit and exchange interactions. In a certain sense, cluster calculations give a better description of the total electronic structure of nonconductive 3*d* oxides than band calculations [20].

The basic centers for the formation of the crystal and electronic structure of the CuO_2/NiO_2 planes in cuprates/nickelates are CuO_4/NiO_4 clusters with the strongest covalence in the series of 3*d* oxides *p-d*-covalence. The electron density in the $[CuO_4]^{5-,6-,7-}$ and $[NiO_4]^{6-,7-,8-}$ charge centers is distributed to varying degrees between the central cation and the ligands, so that they only nominally bind to the $Cu^{3+,2+,1+}$ and $Ni^{2+,1+,0}$ ions, which is especially indicative of „implausible" valence states of the type Cu^{3+} or $Ni^{1+,0}$.

A detailed analysis of the optical and EELS (electron energy loss spectra) spectra of various cuprates [21–25] showed that the most intense low-energy absorption bands with maxima at ≈ 2 eV in cuprates with an T-structure and at ≈ 1.5 eV in cuprates with an T'-structure (bulk samples), which form the fundamental absorption band, are associated with inter-center *d-d* charge-transfer transitions and the formation of so-called *d-d* charge-transfer excitons, which is typical for MH-insulators. The spectra of the real and imaginary parts of the dielectric function ε_{xx} for T-La_2CuO_4 and T'-Nd_2CuO_4 [23] with expansion into Lorentzians (Fig. 1) well illustrate the corresponding exciton peaks. Thus, the minimum energy required for the creation of an electron-hole pair by a direct Franck-Condon (FC) optical transition with charge transfer in the parent cuprates, i.e. optical gap is $E_{\text{gap}}^{\text{opt}} \approx$1.5-2 eV.

The *d-d*-CT excitons in cuprates can be represented as bound spinless electron $[CuO_4]^{7-}$ and spinless hole $[CuO_4]^{5-}$ centers corresponding to a CuO_4 cluster with completely filled Cu 3*d*- and O 2*p* -shells or vacuum state for holes $|0\rangle$, and the two-hole configuration $|2\rangle$ of the CuO_4 cluster with the ground state Zhang-Rice (Zhang-Rice [26]) singlet. The doublet $|02\rangle$, $|20\rangle$ splits due to the resonant two-particle transfer reaction $|02\rangle \leftrightarrow |20\rangle$. New superpositions

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|02\rangle . |20\rangle)$$

with energy $E_\pm = U - V_{\text{EH}} \pm |t_B|$ form dimers of the *S*-($|+\rangle$) and *P*- ($|-\rangle$) type, where U is the energy of formation of a pair of unbound electron and hole centers or the effective parameter of local correlations, V_{EH} is the binding energy of electron and hole centers in parent cuprate or the effective parameter of nonlocal correlations. The value of the effective integral of the two-particle transfer $t_B = \langle 20|H|02\rangle$, which determines the *S-P* splitting, plays a fundamental role in the formation of the unusual superconducting state of cuprates. This integral is actually the transfer integral of an effective local spin-singlet composite boson formed by a pair of holes localized on the same CuO_4 cluster and formally distinguishing between the electron and hole centers [16]. In fact, such a local boson exists only as an indivisible part of the hole ZR center $[CuO_4]^{5-}$ (nominally Cu^{3+}). Independent experimental data for various cuprates indicate that $t_B \approx 0.1$ eV [12] is close, as expected, to the value of the exchange integral in the parent cuprate. All three parameters, U, V_{EH} and t_B will play a fundamental role in the formation of various phase states of cuprates.

Generally speaking, the *d-d* exciton is a fairly stable entity with „length" on the order of 8 Å, which is especially well seen in the linear and nonlinear optical responses for 1D cuprates [27–33]. Quasi-1D cuprates of the Sr_2CuO_3 type with CuO_4 clusters bound through one common anion (corner-sharing) are convenient objects for observing and separating the contributions of intra-center (p-d) and inter-center (d-d) charge-transfer transitions especially by angle-resolved EELS which allows to investigate not only the polarization, but also the dispersion of excitons [21,22,33].

Unlike the P exciton, the S exciton is dipole-forbidden and corresponds to the so-called two-photon state. However, these two excitons have a very strong dipole coupling with an anomalously large value of the dipole moment matrix element:

$$d = |\langle S|\hat{\mathbf{d}}|P\rangle| \approx 2\,e\,R_{\text{CuCu}} \approx 8\,e\,\text{Å}\,. \qquad (1)$$

This indicates a very important role played by the *S-P* doublet in nonlinear optics, in particular, in the effects of two-photon absorption and generation of the third harmonic [27,28]. Indeed, quasi-one-dimensional insulating cuprates Sr_2CuO_3 and Ca_2CuO_3 with CuO_4 centers bound by a common oxygen ion (corner sharing) exhibit anomalously large third-order optical nonlinearities, as evidenced by electroreflection [29,30], third harmonic generation [31], two-photon absorption [27,32]. Model fitting of the nonlinear optical features observed near 2 eV in Sr_2CuO_3,

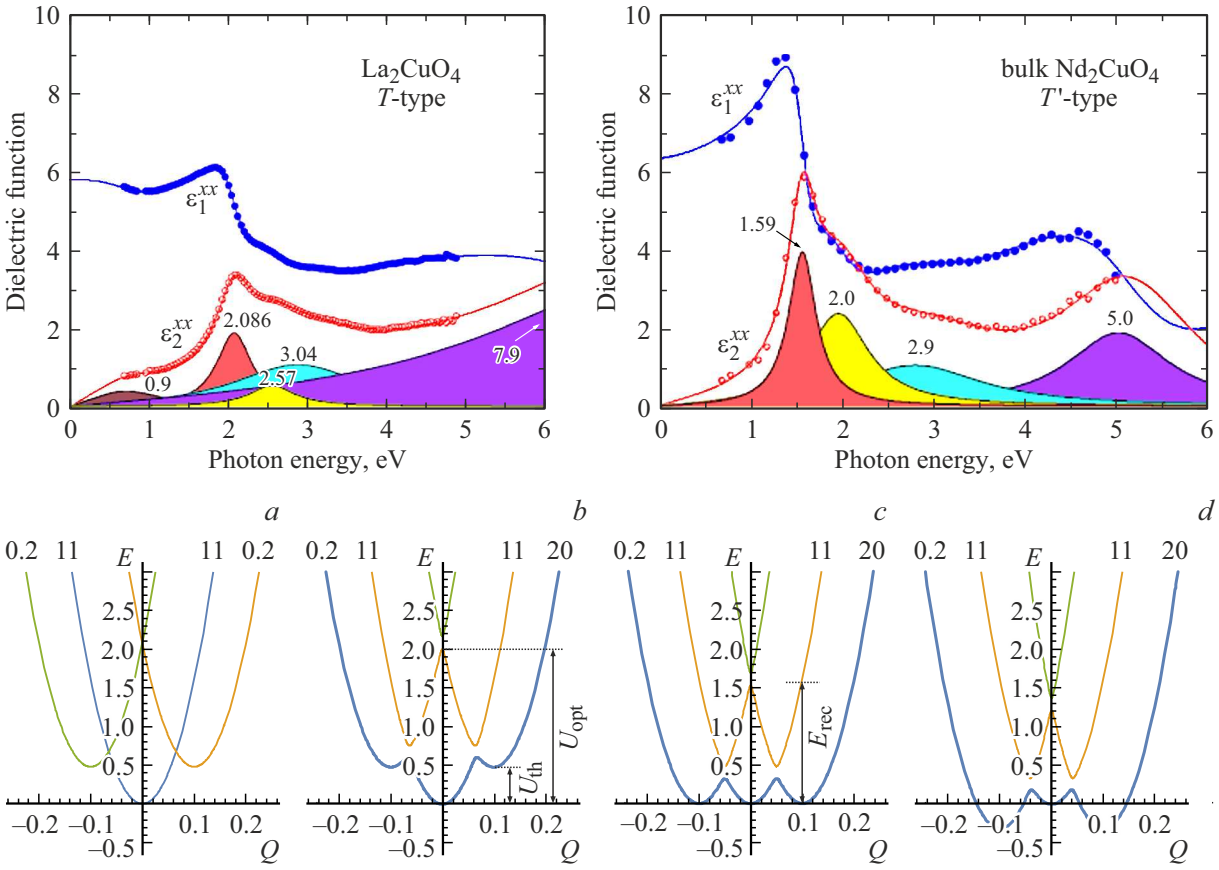

Figure 1. Upper panel: dielectric function spectra for T-La_2CuO_4 and T'-Nd_2CuO_4 [23]. Bottom panel: simplified potential energy curves for „11-02-20–tasks“: *a* — Diabatic potential curves for the „parent“ pair Cu^{2+} - Cu^{2+} — (11) and EH-dimers (20 and 02); *b* — adiabatic potential curves for a pair taking into account the influence of one- and two-particle transport, the optical charge transfer gap U_{opt} corresponds to the energy of the Franck-Condon (FC) CT transition, and the thermal or adiabatic gap U_{th} corresponds to the energy of the non-Franck-Condon (NFC) CT transition. The curves in Fig. *c* and *d* illustrate the result of a formal decrease in the value of U_{opt}.

gives $E_P = 1.74$ eV, $E_S = 1.92$ eV, $\langle S|x|P\rangle = 10.5$ Å [32] (or ≈ 8 Å [29]). Despite some discrepancies in different papers [29,30,32], these parameters are consistent with both theoretical expectations and data obtained in other independent measurements. In other words, nonlinear optical measurements make it possible to reliably estimate both the effective „length“ of a two-center *d*-*d*-CT exciton, and the value of the transfer integral of the composite boson $t_B = \frac{1}{2}(E_S - E_P) \approx 0.1$ eV.

d-*d*-CT excitons can be considered as a peculiar result of photoinduced disproportionation of

$$CuO_4^{6-} + CuO_4^{6-} \rightarrow CuO_4^{7-} + CuO_4^{5-} \qquad (2)$$

with a disproportionation energy or an optical charge transfer gap of the order of 1.5–2.0 eV. This, at first glance, relatively small value of the transfer energy was nevertheless considered as an argument against a number of HTSC mechanisms in cuprates, in particular, the negative U model [34]. However, not short-lived photoinduced *d*-*d*-CT excitons, but low-energy metastable charge excitations above the ground state, coupled electron-hole pairs or *d*-*d*-type EH dimers, which are a direct analogue of *d*-*d*-CT excitons self-trapped as a result of the electron-lattice relaxation. Strictly speaking, the concept of an EH dimer is somewhat broader than that of a self-trapped *d*-*d*-CT exciton, but below, for simplicity, we will consider them to be complete analogues. In contrast to the optical charge transfer gap the energy of formation of an EH-dimer, thermal U_{th} or adiabatic gap can be both a small positive and theoretically even a negative value. Moreover, a (meta)stable EH dimer can always be considered as a system with a negative disproportionation energy, i.e. as a center with negative energy of local correlations (negative-U center). The stability of the EH dimer as a polaron-like center is maintained by the electron-lattice interaction with a specific (half-breathing) displacement mode of the oxygen ion common to the electron and hole centers. Let us note that the formation of low-energy *d*-*d*-type EH dimers is characteristic of MH insulators, while CT insulators will be characterized by *p*-*d*-type EH dimers, which V. Vikhnin called charge transfer vibronic excitons, CTVE [35].

To illustrate the effects of electron-lattice relaxation and evolution of *d*-*d*-CT excitons, the lower panel of Fig. 1 shows simplified potential energy curves for the electron

-vibrational or pseudo-Jahn-Teller „11-02-20−problem“, assuming a single active local conformational mode (half-breathing mode) Q both without (Fig. 1, a) and with charge transfer effects (Fig. 1, b, c, d) . Arrows indicate direct Franck-Condon FC transitions with charge transfer and energy $U_{\rm opt}$, occurring under „frozen“lattice conditions, photo-recombination transition, as well as weak „non-Franck-Condon“NFC transitions with energy $U_{\rm th}$, the final state of which corresponds to a relaxed lattice. The emergence of „bistability“, with stable EH-dimers that can compete with the „parent“ configuration $|11\rangle$ ($[CuO_4]^{6-}+[CuO_4]^{6-}$) in the „struggle“for the ground state, is a fundamental feature of cuprates.

Figures 1, a, b describe the situation typical for parent antiferromagnetic insulating T cuprates with $U_{\rm opt}\approx 2.0$ eV, $U_{\rm th}\approx 0.5$ eV, when magnetic $s = 1/2$ centers $[CuO_4]^{6-}$ form the ground state. Fig. 1, c illustrates the dramatic effect of a relatively small decrease in the value of $U_{\rm opt}$ from $\sim$2 eV to $\sim$1.5 eV as a result of the influence of a change in the out-of-plane out-of-plane stuff, or due to screening of local correlations as a result of doping, at which $U_{\rm th}$ becomes close to zero or even a small negative, so that the system becomes unstable with respect to disproportionation $11 \to 20\,(02)$ with the opportunity of a fundamental change in the ground AFMI state to new states initiated by the system of EH dimers, and possibly to the Fermi liquid state. Generally speaking, in this case, all three components of the charge triplet $[CuO_4]^{5-,6-,7-}$ should be considered on the equal footing. This unique „quasi-degeneracy“ situation is predicted for parent cuprates with an T' structure without „apex“ oxygen. Indeed, optical ellipsometric measurements [23] for single-crystals of parent dielectric antiferromagnetic cuprates T'-R_2CuO_4 (R = Pr, Nd, Sm) indicate the value $U_{\rm opt}\approx 1.54$-1.59 eV, which is approximately 0.5 eV less than in T-La_2CuO_4 (Fig. 1).

With a further decrease in the optical charge transfer gap $U_{\rm opt}$ (Fig. 1,d), we switch to the regime of significantly negative values of $U_{\rm th}$, the regime of complete disproportionation, when the ground state of the CuO_2-planes will be formed by a system of both bound (EH-dimers) and individual electron and hole centers, i.e. non-magnetic charge doublet $[CuO_4]^{5-,7-}$.

In accordance with Fig. 1, it can be argued that in the parent cuprates with T structure, with a relatively small positive value of $U_{\rm th}$ „the struggle“ for the ground state is nevertheless won by the insulating AFMI phase. In parent cuprates with T' structure, the value of $U_{\rm th}$ is apparently close to zero, which leads to a critical closeness of the free energies of the insulating AFMI phase and the phases formed by a system of electron and hole centers, in particular, the superconducting phase. Obviously, parent T' cuprates are located directly near the disproportionation threshold and transition to the system of EH dimers. The dielectric AFMI state in bulk samples of these cuprates is stabilized by residual „apex“ oxygen, which cannot be completely removed [9]. Improvement in the deposition and annealing technique made it possible to obtain thin films of parent T'-cuprates R_2CuO_4 (R = Pr, Nd, Sm, Eu, Gd) practically without „apex“ oxygen, which are metallic at high temperatures and superconducting at temperatures ≤ 30 K [9]. In other words, in cuprates with an ideal T' structure, it is possible to implement the regime of negative values of the local correlation parameter U („negative-U “ regime).

Obviously, the phase diagrams of apexless nickelates can also be explained under the assumption of small negative $U_{\rm th}$, at which the insulating phase with long-range AFMI order becomes energetically unfavorable, although its „traces“ will be observed in the form of well developed antiferromagnetic fluctuations [36].

Unfortunately, experimental information on the effective parameters of local and nonlocal correlations of $U_{\rm th}$ and $V_{\rm EH}$ is extremely scarce. Thus, high-temperature Hall measurements made it possible to estimate the formation energy of a pair of unbound electron and hole carriers in the parent T cuprate La_2CuO_4 [37]: $\Delta_{\rm EH} = U_{\rm th} + V_{\rm EH} = 0.89$ eV. Measurements of the chemical potentials of holes and electrons in $Y_{0.38}La_{0.62}Ba_{1.74}La_{0.26}Cu_3O_y$ (YLBLCO) [38] give a value of the order of 0.8 eV for this energy. This means that the energy $U_{\rm th}$ of formation of electron and hole centers bound in the EH dimer should be significantly less than 0.8−0.9 eV, which indicates the instability of the parent cuprates with respect to charge transfer with the formation of stable EH dimers. This energy can be identified as the low-energy edge of the weak NFC band, clearly visible in the mid-infrared (MIR) range 0.4−1.0 eV in all parent cuprates [39–41] and in a certain sense being their visiting card. Taking into account the value $U_{\rm th}\approx 0.4$ eV, which is confirmed by various experimental data [12,42–44], we obtain the value $V_{\rm EH}\approx 0.5$ eV for the binding energy of electron and hole centers in La_2CuO_4. Let us pay attention to the data of the work [45], according to which the energy of formation of a pair of unbound electron and hole carriers in the parent T' cuprate Nd_2CuO_4 is only 0.5 eV, which implies, as expected, the value $U_{\rm th}$ close to zero.

It should be noted that a narrow peak associated with two-magnon (2M) absorption formed upon spin flip of neighboring centers is found at the edge of a rather wide MIR band in T cuprates. In the spin-wave approximation, this energy is estimated as $E_{\rm 2M} = 2.73\,J \approx 0.3$-$0.4$ eV [39]. By the way, such a two-magnon peak is the only spectral feature in the MIR range of the antiferromagnet La_2NiO_4 [39] isostructural to cuprates, which emphasizes the uniqueness of cuprates as systems that are unstable with respect to charge transfer and the formation of stable EH dimers, as well as the close energies of charge (but neutral!) and magnetic excitations.

An important argument in favor of the existence of metastable EH dimers in parent cuprates is the discovery of relatively weak but distinct peaks in the optical conductivity of $Sr_2CuO_2Cl_2$ [46] and $YBa_2Cu_3O_6$ [41] at $E = 1570\ {\rm cm}^{-1}$ (0.195 eV) and $E \approx 1600\ {\rm cm}^{-1}$ (0.2 eV), respectively, which can be uniquely associated with S-P transitions in EH

dimers. These data give an independent estimate of the transfer integral of the composite boson $t_B \approx 0.1$ eV.

EH dimers manifest themselves in different optical properties of the parent cuprates. Thus, in the photoinduced absorption spectra of La_2CuO_4 , there are two distinct features at 0.5 and 1.4 eV [47], which are naturally attributed to photodissociation and photorecombination for photoinduced EH dimers, respectively [12, 42 ,25]. There were similar effects in Nd_2CuO_4 [48], $YBa_2Cu_3O_{6.2}$ [49], $Sr_2CuO_2Cl_2$ [50].

4. EH dimers, charge triplets, and phase diagram of cuprates and nickelates

The anomalously high electrical polarizability of EH dimers, which can be considered as the nucleation centers of a new highly polarizable phase, the transition to which of thr polarization unstable parent phase can be either spontaneous or induced, for example, by nonisovalent substitution, is of fundamental importance for cuprates.

The high-temperature phase in cuprates and nickelates is characterized by the competition of magnetic and charge fluctuations in „struggle“ for the low-temperature ground state. With a relatively simple short-range magnetic order in parent cuprates and nickelates with a single characteristic energy J (exchange integral), the formation of an antiferromagnetic Néel state with a decrease in temperature is associated, while charge fluctuations, depending on the ratio between the parameters of local and nonlocal correlations, one- and two-particle transfer integrals, as well as the parameters of the electronic-vibrational interaction, can lead to the formation of a non-magnetic insulating phase or charge ordering (CO), a coherent metallic Fermi liquid FL phase, a bosonic superconducting (BS) phase, as well as a specific EH dimer phase [11–16]. In La_2CuO_4 with T-structure, this struggle is won by magnetic fluctuations, which form an antiferromagnetic insulating phase. A similar situation is observed in bulk samples of Nd_2CuO_4 with an irremovably low content of apex oxygen ions, while in thin films of Nd_2CuO_4 with an almost ideal apexless T' structure, the „victory“ remains behind charge fluctuations of the type of EH-dimers, which are the centers of formation of the ground nonmagnetic superconducting state with $T_c \approx 30$ K [9]. The long-range magnetic order is also absent in „parent“ nickelates $RNiO_2$, and the charge subsystem exhibits complex behavior from insulating, weakly insulating and metallic to superconducting with nonisovalent doping. Thus, the temperature dependence of the resistance in $LaNiO_2$ indicates a metallic state at high temperatures with insulating upturn at low temperatures, which is typical for cuprate La_2CuO_4 at low hole doping [51].

At finite temperatures, parent cuprates are systems with a low concentration of metastable EH dimers, whose giant electrical polarizability leads to anomalous behavior of cuprates upon nonisovalent substitution in systems of the type $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$, $YBa_2Cu_3O_{6+x}$ and $La_2CuO_{4+\delta}$, accompanied by the appearance of a inhomogeneous electric potential and electron or hole doping. An increase in the concentration of impurity electric potential centers upon nonisovalent substitution is accompanied by condensation and an increase in the concentration of EH dimers, which ensure effective screening of the impurity potential. This is evidenced, in particular, by the data [46] of measurements of infrared spectra of cuprates $Sr_{2-x}CuO_2Cl_2$, $Y_{1-x}Ca_xBa_2Cu_3O_6$, $Bi_2Sr_{2-x}La_xCuO_6$ in a wide range of hole doping $0 < p < 0.18$ [46]. At $p = 0.005$, all samples exhibited a relatively weak narrow peak at ≈ 0.2 eV, which can be unambiguously attributed to S-P transitions in isolated EH dimers with energy $\approx 2|t_B|$. One of the most striking evidence in favor of a sharp increase in the concentration of nonmagnetic EH dimers upon nonisovalent substitution in parent cuprates is the data of the zero field NMR studies on copper nuclei in $Y_{1-x}Ca_xBa_2Cu_3O_6$ [52]. Surprisingly, the substitution of only one Y^{3+} ion for Ca^{2+} led to the appearance of approximately 50 inactive in NMR, i.e. non-magnetic, copper ions.

In favor of the special role of d-d-CT-excitons and EH dimers is the observation of the effects of non-stationary (transient) and „frozen“ (persistent) photoconductivity using both visible light and various lasers (argon, krypton, helium-neon), as well as photoinduced superconductivity in dielectric cuprates of systems 123 and 214 near the transition to the superconducting state [53–55]. Obviously, a photoinduced increase in the concentration of EH dimers, and not just photoexcitation of additional mobile holes [53–55], can naturally explain these effects.

Simultaneously with an increase in the concentration of EH dimers, there is a sharp decrease in the binding energy of electron and hole centers in EH dimers. Thus, according to the data of high-temperature Hall measurements [37] the energy of formation of a pair of unbound electron and hole carriers Δ_{EH} sharply decreases from 0.89 to 0.53 eV when only 1% of trivalent La^{3+} ions are replaced by divalent Sr^{2+} ions in the parent cuprate La_2CuO_4 and continues to drop sharply with a further increase in doping. Obviously, this effect is due to the strong screening of the parameters of local (U_{th}) and nonlocal (V_{EH}) correlations in EH dimers [43,44], which leads to the suppression of the AFMI phase and the shift of the phase equilibrium towards a system of strongly correlated electron and hole centers, equivalent to a Bose liquid [11–16] with the opportunity of forming a superconducting Bose-Einstein condensate at some critical doping value. The long-range antiferromagnetic order in $La_{2-x}Sr_xCuO_4$ is already destroyed at $x \approx 0.02$ with a transition to the spin glass phase.

Thus, the real situation in both parent and doped cuprates/nickelates suggests consideration of a system of CuO_4/NiO_4 centers in the CuO_2/NiO_2 planes, which can be in three different valence charge states with close energies: $CuO_4^{7-,6-,5-}/NiO_4^{8-,7-,6-}$. This charge triplet, following Rice and Sneddon [56], can be formally associated with

the three pseudospin $S = 1$ states with projections M_S = -1, $M_S = 0$ $M_S = +1$ respectively. In charge triplet model [11–16,57] to describe low energy physics, we restrict ourselves to taking into account the lower orbital singlet states of the triplet components (A_{1g}, B_{1g}, A_{1g} respectively [15,16]). Unlike spinless electron (CuO_4^{7-}/NiO_4^{8-}) and, presumably, Zhang-Rice hole (CuO_4^{5-}/NiO_4^{6-}) centers for parent centers (CuO_4^{6-}/NiO_4^{7-}) ordinary spin $s = 1/2$, so we extend the local Hilbert space of the charge triplet model from a pseudospin triplet to a spin-pseudospin $|SM_S s\mu\rangle$ quartet of states: $|1100\rangle$, $|1–100\rangle$, $|10\frac{1}{2}\frac{1}{2}\rangle$, $|10\frac{1}{2}-\frac{1}{2}\rangle$.

The effective spin-pseudospin Hamiltonian of the charge triplet model includes the main interactions: local and nonlocal correlations, three types of correlated one-particle transfer, two-particle (bosonic) transfer, and Heisenberg spin exchange.

As for ordinary spin-magnetic systems, we can integrate out high-energy degrees of freedom and, after projecting onto the selected local spin-pseudospin quartets $|SMs\mu\rangle$, obtain the effective spin-pseudospin Hamiltonian of the cuprate/nickelate CuO_2/NiO_2 plane in the form [11–16]

$$\hat{H} = \hat{H}_{\rm pot} + \hat{H}^{(1)}_{\rm kin} + \hat{H}^{(2)}_{\rm kin} + \hat{H}_{\rm ex}\,, \tag{3}$$

$$\hat{H}_{\rm pot} = \sum_i (\Delta S^2_{iz} - \mu S_{iz}) + \frac{1}{2}\sum_{ij} V_{ij} S_{iz} S_{jz}\,, \tag{4}$$

$$\hat{H}^{(1)}_{\rm kin} = -\sum_{i<j}\sum_{\nu}[t^p_{ij}\hat{P}^{\nu}_{i+}\hat{P}^{\nu}_{j-} + t^n_{ij}\hat{N}^{\nu}_{i+}\hat{N}^{\nu}_{j-} + \frac{1}{2}t^{pn}_{ij}(\hat{P}^{\nu}_{i+}\hat{N}^{\nu}_{j-} + \hat{P}^{\nu}_{i-}\hat{N}^{\nu}_{j+}) + h.c.]\,, \tag{5}$$

$$\hat{H}^{(2)}_{\rm kin} = -\sum_{i<j} t^b_{ij}(\hat{S}^2_{i+}\hat{S}^2_{j-} + \hat{S}^2_{i-}\hat{S}^2_{j+})\,, \tag{6}$$

$$\hat{H}_{\rm ex} = \frac{1}{4}\sum_{i<j} J_{ij}\boldsymbol{\sigma}_i\boldsymbol{\sigma}_j\,, \tag{7}$$

where Fermi-type operators $\hat{P}^{\nu}_{\pm}$ and $\hat{N}^{\nu}_{\pm}$, associated with pseudospin raising/lowering operators $\hat{S}_{\pm}$ and $\hat{T}_{\pm} = \{\hat{S}_z, \hat{S}_{\pm}\}$ and obeying to anticommutation permutation relations, change both the local charge (pseudospin) and spin states, acting as follows:

$$\hat{P}^{\nu}_{+}|10;\tfrac{1}{2}-\nu\rangle = |11;00\rangle, \quad \hat{P}^{\nu}_{-}|11;00\rangle = |10;\tfrac{1}{2}-\nu\rangle,$$

$$\hat{N}^{\nu}_{+}|1-1;00\rangle = |10;\tfrac{1}{2}\nu\rangle, \hat{N}^{\nu}_{-}|10;\tfrac{1}{2}\nu\rangle = |1-1;00\rangle,$$

$\boldsymbol{\sigma} = 2\hat{P}_0\mathbf{s}$, $\hat{P}_0 = 1 - \hat{S}^2_z$ — the operator of local spin density. The $\hat{S}^2_{\pm}$ raising/lowering operators change the projection of the pseudospin onto ± 2 and describe the transitions „electronic $\leftrightarrow$ hole“ centers, i.e. are the creation/annihilation operators of a hole pair as an effective local composite boson. The average

$$\Psi = \langle S^2_{\pm}\rangle = \frac{1}{2}(\langle S^2_x - S^2_y\rangle \pm i\langle\{S_x, S_y\}\rangle$$

can serve as d-symmetric parameter of local superconducting order.

The first term in $\hat{H}_{\rm pot}$ describes local correlation effects ($2\Delta = U$), in the second term μ is chemical potential, the last term in (2) describes nonlocal inter-center correlations. The Hamiltonian $\hat{H}^{(1)}_{\rm kin}$ describes three types of the single-particle correlated transport, and the Hamiltonian $\hat{H}^{(2)}_{\rm kin}$ is two-particle transport or transfer of effective composite bosons.

In the Hamiltonian (3) we actually limited ourselves by the approximation of frozen lattice, whereas, strictly speaking, this Hamiltonian should include not only the electron-vibrational interaction, but also the impurity potential in cuprates/nickelates with nonisovalent substitution, which generally plays an important role in the formation of inhomogeneous electronic state.

Using the well-known effective field theory (EFT) for spin magnets, which combines the molecular field approximation (MFA) with accurate accounting of the local correlations, the variational approach (VA) based on the Bogolyubov inequality for a grand potential, and the Caron-Pratt model for the local coordinate description of the Fermi liquid FL phase [58], we were able to numerically calculate the phase diagrams of the complete spin-pseudospin system for the CuO_2/NiO_2 planes within a simplified model (doping-independent parameters, two sublattices, nearest neighbor approximation,...) [15,16]. For illustration, Fig. 2 shows a series of 2D EFT phase diagrams calculated with constant values of the parameters of the effective spin-pseudospin Hamiltonian [14–16]. The upper panel (a)–(d) shows the phase diagrams assuming the presence of the main homogeneous phases NO, AFMI, BS, CO, FL without taking into account the effects of phase separation.

The phase diagram presented in Fig. 2, a, is calculated for rather arbitrarily chosen parameters (insert in Fig. 2, a), but with their ratio leading to complete suppression of the AFMI and CO phases in favor of the BS phases and FL, which form the ground state of the planes CuO_2/NiO_2 at $0 \le n \le 0.16$ and $n > 0.16$, respectively. Such phase diagrams without traces of long-range AFMI- and CO-ordering turn out to be typical for cuprates with an ideal or almost ideal T' structure [9], and also, possibly, for nickelates, which also lack apex oxygen [2]. Although the AFMI phase is energetically unfavorable for the chosen values of the Hamiltonian parameters, its energy differs little from the energy of the BS and FL phases, so that the slightest increase in the value of the exchange integral by 1% or a corresponding decrease in the remaining parameters is sufficient to restore the AFMI phase, although in a small area of the $T - n$ phase diagram (Fig. 2, b). Naturally, with a further increase in the exchange integral, the region of the AFMI phase increases up to the BS-AFMI transformation of the ground state for the parent composition (Fig. 2, c). Thus, a relatively small change in parameters can radically change the phase diagram. Interestingly, a similar effect of suppression/restoration of the AFMI phase is observed

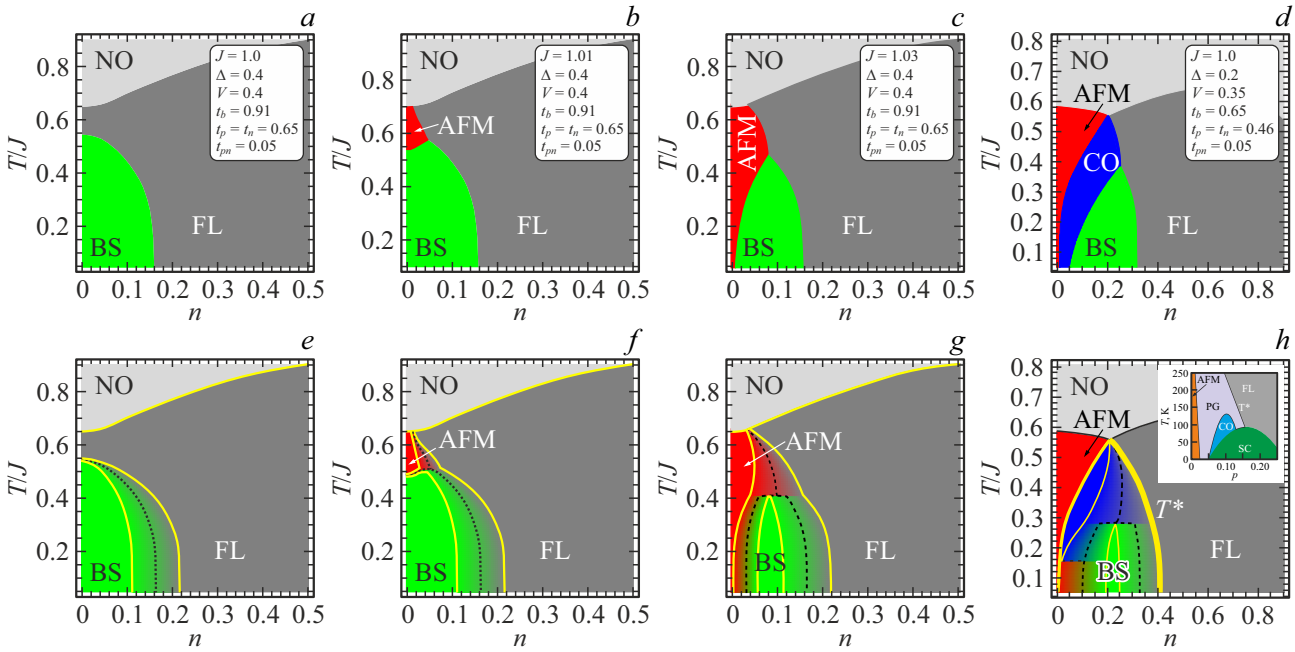

Figure 2. Model phase diagrams T-n of hole-doped CuO_2/NiO_2 planes in cuprates/nickelates, calculated in the effective field approximation ($n = p$ for hole doping) with constant values of the Hamiltonian parameters: J — exchange integral, $\Delta = U/2$ — parameter of local correlations, V — parameter of non-local correlations, t_p, t_n, t_{pn} — three independent integrals of correlated single-particle transfer, t_B — effective integral of composite boson transfer (see inserts) assuming competition between „monophases“ NO (disordered), AFMI, BS, FL, CO [16]. The upper panel (a)–(d) shows the phase diagrams assuming the presence of the main homogeneous phases without taking into account the possible coexistence of two adjacent phases. The boundaries between the phases represent lines of equality of free energies. The lower panel (e)–(h) shows the phase diagrams, taking into account the phase separation, calculated using the Maxwell construction. The dashed curves on (e)–(h) indicate the line of equal volume fractions of two adjacent phases, the yellow curves on (e)–(h) represent the lines of phase transitions „of the third“ kind, limiting the areas with a limiting 100% volume fraction of one of the phases.

in T' cuprates at the slightest change in the concentration of nonstoichiometric apex oxygen [9], accompanied by a corresponding change in the external potential for CuO_2-planes. With a twofold decrease in the parameter of local correlations $\Delta = U/2$ with a relatively small change in the remaining parameters, the ground EFT state of the model plane CuO_2/NiO_2 can demonstrate a series of successive transformations AFMI–CO–BS–FL with a deviation from half-filling (Fig. 2, d), surprisingly resembling the situation in real cuprates with hole doping (insert in Fig. 2, h).

However, the numerical implementation of Maxwell construction shows that the minimum of the free energy in the region of coexistence of phases AFMI-FL, AFMI-BS, CO-BS, CO-FL and BS-FL, separated by lines of phase transitions of the first order, corresponds to phase separation (PS). The phase diagrams with allowance for the phase separation presented in the lower panel of Fig. 2 indicate a more complex nature of the transformation of the phase states in the model cuprates/nickelates. In particular, this concerns the manifestation of percolation effects, including the percolation nature of the superconducting transition, effects of local superconductivity, a whole series of characteristic temperatures, lines of phase transitions of the „third kind“, enclosing regions with a limiting 100% volume fraction of one of the phases. The mysterious pseudogap phase turns out to be nothing more than a PS state AFMI-FL-CO-BS bounded by a third-order phase transition line $T^*(n)$ (pseudogap temperature) that separates the gapless 100% metallic FL phase from the gaped AFMI, CO, and BS phases (Fig. 2, h).

The phase diagrams shown in Fig. 2 convincingly show that the ground state and the $T-n$ phase diagrams of the model cuprate/nickelate are, generally speaking, determined by the ratio between the values of all parameters characterizing local and nonlocal correlations, one- and two-particle transport, and spin exchange .

In accordance with the conclusions of the paper [59], we can state that the metallic FL phase in cuprates/nickelates is responsible for many unusual properties of the normal state (quantum oscillations, „Fermi arcs“, features of the angle resolved photoemission spectra ARPES, ...), but is not directly related to the formation of the superconducting state. High-temperature superconductivity in cuprates/nickelates has nothing to do with „pairing“ of doped carriers, but is a consequence of the condensation of effective composite bosons.

The electron-hole nature of the superconducting phase of cuprates manifests itself, in particular, in experiments

to study the effect of optical „Cooper pair breaking“, (CPB) [60,61]. This is indicated by a rather sharp CPB resonance at 1.5 eV in the optical spectrum of the superconducting system 123 which it is natural to associate not with the existence of antiferromagnetic regions in the superconducting phase [61], but with the recombination of electron-hole centers, which destroys the bosonic superconductivity. Thermal modulation spectroscopy (TMS) data [62] can also be associated with the same effect. A sufficiently high recombination energy determines the stability of the superconducting phase with respect to its transformation into the initial dielectric antiferromagnetic phase.

5. Conclusion

The concept of *d-d* charge-transfer excitons in the insulating antiferromagnetic phase of cuprates and metastable low-energy EH dimers as a result of their evolution, taking into account electron-lattice relaxation, turns out to be very fruitful not only for describing linear and nonlinear optical properties and photoinduced effects, but also to develop a promising model of charge triplets to describe the low-energy electronic structure of the CuO_2 or NiO_2 active planes and its evolution under both doping and changing the main energy parameters.

An analysis of the effective spin-pseudospin Hamiltonian of a system of charge triplets in the framework of the effective field theory indicates the possibility of describing phase diagrams typical both for cuprates with an T- or T' structure and for nickelates of the $RNiO_2$ type. Among the fundamental conclusions of the model of charge triplets, we note:

– the metallic FL phase in cuprates/nickelates is responsible for many of the unusual properties of the normal state, but is not directly related to the formation of the superconducting state;

– high-temperature superconductivity in cuprates/nickelates is a consequence of the condensation of effective composite bosons and is not related to „pairing“ of the doped carriers;

– the pseudogap phase in cuprates is the region of phase separation AFMI-FL-CO-BS, limited by the line of the phase transition „of the third“ kind.

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Conflict of interest

The author declares that they have no conflict of interest.

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