Peculiarities of the Electronic Structure and Optical Spectra of Mott Insulator Nanoparticles

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Abstract—Changes in the electronic structure of Mott insulators upon transition from bulk crystals to nanoparticles have been considered. It is shown that an increase in the concentration of surface defects (in particular, oxygen vacancies for particles of transition metal oxides) leads to the formation of in-gap states of the spin–polaron origin inside the gap. As a result, the optical absorption spectrum of a nanoparticle undergoes a red shift with respect to a crystal.

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INTRODUCTION

At the transition from classical bulk semiconductors and insulators to nanoparticles, it is reasonable to expect band gap broadening and, consequently, a blue shift of the fundamental absorption edge. This effect is well described within the simplest one-electron band model as a result of quantum confinement [1]. Specifically this shift was observed in the Cu$_2$O semiconductor, whose electronic structure is adequately described by the band theory. Different behavior was observed for nanoparticles of materials with strong electron correlations (SECs), e.g., for copper monoxide CuO. In this case, a pronounced red shift was observed at the transition from bulk materials to nanoparticles [2]. In this study, we theoretically discuss the changes in the electronic structure and optical spectra of Mott insulators at the transition from bulk crystals to nanoparticles with the multi-electron approach—the generalized tight-binding (GTB) method, which was previously developed by us to describe high-temperature superconducting (HTSC) cuprates [3]. The GTB method predicts formation of in-gap levels with a high state density for doped Mott insulators and, consequently, appearance of optical density at energies lower that the fundamental absorption edge $E_g$. The experimental data on the optical absorption spectra of CuO nanoparticles [2] are analyzed within the multi-electron approach. The conclusions drawn in this study are also applicable to nanoparticles of HTSC electronic cuprates Nd$_{2-\delta}$Ce$_x$CuO$_4$.

Experimental study of CuO nanoparticles by different methods revealed increased number of an oxygen vacancies and concentration of Cu$^+$ ions in comparison with bulk CuO [2]. From the viewpoint of the electronic structure of a Mott–Hubbard insulator (to which CuO belongs), the same defects cause electron doping. As in layered HTSC cuprates, doping leads to the formation of in-gap states. Let us consider in more detail the mechanism of this formation as applied to CuO.

BASIC CONCEPTS OF THE GTB METHOD

Calculation within the GTB method is performed in three stages [3].

(i) lattice is divided into a set of unit cells; in each cell, the Hamiltonian is written in the Wannier function representation for orthogonalization of the states of the neighboring cells. Then, accurate numerical diagonalization of the Hamiltonian of a cell is performed and multielectron orbitals with numbers of electrons $N_e$ and $N_e \pm 1$ are built. The number $N_e$ is derived from the electroneutrality condition. For example, in the case of cuprates, due to the almost complete $d$-band occupation, it is convenient to work in the hole representation; thus, for undoped CuO, $n_h = 1$ (i.e., one hole per cell). As a unit cell, a CuO$_4$ cluster can be chosen; because of the electroneutrality of the crystal in the stoichiometric case, we can ascribe the valences Cu$^{2+}$O$^{2-}$ to ions. We will enumerate the multi-electron terms of a cell by the number of holes; in particular, in the $3d^{10}2p^n$ configuration, we have a hole per cell; $n_h = 1$. Addition of an electron leads to the formation of the $3d^{10}2p^{n+1}$ configuration with $n_h = 0$ (Cu$^+$ ion). Addition of a hole induces two-hole terms with $n_h = 2$ described by superposition of the $3d^{10}2p^6$, $3d^{10}2p^5$, $3d^{10}2p^42p^3$, and $3d^{10}2p^4$ configurations (Cu$^{3+}$ ions appear with a finite probability).

(ii) In the second stage, the Hubbard operators of a cell are built in the basis of multi-electron wave functions of a cell |$p$> according to the standard definition: $X^{pq} = |p$$><q|$, and all the local operators (Fermi, spin, and other possible) are written in the Hubbard operator representation.
(iii) At the third stage, remaining interactions and hops between cells are written in the $X$-operator representation and taken into account according to the perturbation theory. Within this representation, the Hamiltonian of the multiband $p–d$ model, containing the cation $d$ electrons and anion $p$ electrons is exactly expressed as the Hamiltonian of the Hubbard model in the $X$ representation. Different variants of the perturbation theory, from very simple decoupling procedure to the complex diagram technique for the $X$ operators are described in the monograph [3].

### X OPERATORS AND PERTURBATION THEORY

Exactly the same CuO$_4$ cluster was considered in the GTB method applied to calculations of the electronic structure of Nd$_3$CuO$_4$ ($n$-type HTSC) [4]. Figure 1 schematically shows three orthogonal subspaces of the Hilbert space with the number of holes $n_\sigma = 0(n_0)$, $1(n_1)$, and $2(n_2)$ and the multielectron terms $E_0(S = 0)$, $E_{1\sigma}(S = 1/2, \sigma = \pm 1/2)$, and $E_2(S = 0)$. The spin doublet $E_{1\sigma}$ is shown split by the internal two-sublattice molecular field; the spin sublevel filled at $T = 0$ is denoted by a cross. The arrows indicate the one-particle Fermi excitations; each of them is described by its own Hubbard operator (in the case of addition of an electron, the band index “0” corresponds to the bottom of the conduction band, $\Omega(c)_\sigma = E_\sigma − E_0$ and, in the case of addition of a hole, the band index “1” corresponds to the top of the valence band, $\Omega(o)_\sigma = E_\sigma − E_{1\sigma}$, where $\Omega = −\sigma$. The gap between the filled valence band and empty conduction band (in this case, a charge-transfer gap) is $E_{\gamma_0} = \Omega(c) − \Omega(o) = 2E_{1\sigma} − E_0 − E_2$ at the parameters $E_{\gamma_0} = 2$ eV, which are typical of cuprates. The only difference between Nd$_3$CuO$_4$ and CuO, from the viewpoint of the theory of their electronic structures, is in the way of three-dimensional unit-cell packing of, which should certainly manifest itself in the difference between the dispersion relations of electronic quasi-particles near the top of the filled valence band and the bottom of the empty conduction band. However, even in a single crystal, dispersion is small, with a typical width of about 0.3–0.4 eV; therefore, we can neglect hops for nanoparticles.

The physical mechanism of the formation of new in-gap states upon $n$-type doping can be easily explained using the diagram in Fig. 2. Upon such doping (let $x$ be the concentration of Cu$^+$ ions), the occupation numbers of the terms shown in Fig. 1 change (they are determined by solving the self-consistency equation for the chemical potential). At $T = 0$, we obtain

\[ n_0 = x, \quad n_{1+} = 1 - x, \quad n_{1-} = 0, \quad n_2 = 0. \tag{1} \]

Each quasi-particle in the GTB method is characterized not only by an energy but also by a spectral weight, which is determined by the sum of the occupation numbers of the initial and final multielectron terms. Thus, upon doping, the spectral weights of the $\Omega(c)$ and $\Omega(o)$ bands are redistributed:

\[ F_0 = 1 - x + x = 1, \quad F_1 = 1 - x, \tag{2} \]

and a new quasi-particle arises, whose spectral weight is proportional to the doping level (shown by the solid arrow with the band index 2 in Fig. 2).

\[ \Omega_2 = E_{1,\sigma} − E_0, \quad F_2 = x. \tag{3} \]

This is the in-gap state induced by $n$-type doping. In the hole representation, $\Omega_2$ lies above $\Omega_0$ by a magnitude of the internal molecular field $J$. In the electron representation, the in-gap state lies within the gap close to the bottom of the conduction band. The transition from the top of the valence band to empty in-gap states will yield a peak in the absorption spectrum, which is split off from the absorption edge $E_{\gamma_0}$ by a value of about $J$. For cuprates, $J$ is 0.1 eV. The peak intensity is proportional to the doping level, i. e., to the concentration of Cu$^+$ ions and oxygen vacancies. On the basis of these considerations, one may suggest that the absorption bands in the energy range 1.0–1.35 eV, lying directly below the fundamental absorption edge of “unexcited” CuO, which were found in nanostructured CuO samples in [2], belong to the in-gap states split-off from the conduction band.

### DISCUSSION

Note that our consideration assumes removal of the degeneracy of spin sublevels of the hole states. In a bulk crystal, this occurs in the antiferromagnetic phase with...