

Theoretical Model for Optical Spectrum and Structural Dynamics of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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Abstract

Superconductivity in cuprates cannot be fully understood using free-electron theory and the BCS model. Experiments during the last thirty years have shown that structural dynamics and localization cannot be ignored. The Marcus model is applied here for a theoretical assignment of the optical spectra. Hubbard-U absorption at ≈ 2 eV is assigned as metal/metal (MM) charge transfer transition of type $2\text{Cu(II)} + h\nu \rightarrow \text{Cu(I)} + \text{Cu(III)}$. The mid-infrared (MIR) sharp line at 0.35 eV in La_2CuO_4 is interpreted as a vibrational transition with intensity borrowing from the crossing $\text{Cu(I)} + \text{Cu(III)}$ energy curve. Hole-doping decreases U, since holes become available as acceptors. The relationship between the pseudogap and U in the doped cuprate is discussed. The absorption at 0.13 eV and the activation energy at 0.035 eV, existing only after doping, are very likely due to vertical and adiabatic electron exchange of type $\text{Cu(III)} + \text{Cu(II)} \rightarrow \text{Cu(II)} + \text{Cu(III)}$. The pseudogap involves two-electron states.

Keywords: Cuprates, superconductivity (SC), doping, vibronic states, Hubbard-U, MIR absorption, pseudogap, metal-metal charge transfer

1. Introduction

Impressive progress towards an understanding of superconductivity (SC) in cuprates has been made since the discovery in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in 1986 (Bednorz & Müller, 1986). Experimental methods which directly probe the electronic and vibrational wave functions have been advanced (Herr et al., 1987; Preyer et al., 1989; Tokura et al., 1990; Uchida et al., 1991; Thomas, Rapkine, Cooper, Cheong, & Cooper, 1991; Thomas et al., 1992; Perkins et al., 1993). Theoretical progress has been hampered by the desire to keep as much as possible from the Bardeen-Cooper-Schrieffer (BCS) picture, including the free-electron model of electrons. However, vibrational and electronic coordinates interact in a localized way. Delocalization results only “after” this interaction is included, if $x > 0.05$ (Larsson, 1989).

Various spectroscopies, such as absorption spectroscopies, photo-induced charge transfer in the infrared and visible region demonstrate localization very clearly. The pure cuprate La_2CuO_4 ($x=0$) is a Mott insulator and has very little absorption in the low-energy region below 1.7 eV, except a mysterious weak absorption at 0.3 - 0.5 eV in the mid-infrared (MIR) region (Perkins et al., 1993). Strong and wide absorption starts at about 1.8 eV, commonly accepted as due to charge transfer, but there is no agreement on which type of charge transfer. However, this is of crucial importance for the understanding of SC.

The present author suggested already in 1989 (Larsson, 1989) that the Marcus model (Marcus, 1964; Hush, 1967; Reimers & Hush, 2004; Kestner, Logan, & Jortner, 1974; Jortner, 1976; Jortner & Bixon, 1969; Brunschwig, Logan, Newton, & Sutin, 1980; Larsson, 1981; Klimkåns & Larsson, 2000), if applied to electron pairs, would be a useful model for SC in cuprates. In the Born-Oppenheimer approximation the free energy of the “spin-coupled” $\text{Cu(II)}/\text{Cu(II)}$ state and the “charged” $\text{Cu(I)}/\text{Cu(III)}$ state form a common potential energy surface, consisting of two interacting paraboloids with partly common vibrational states (Larsson, 1989).

Conductivity in doped cuprates and CuO (Heikes & Johnston, 1957; Larsson, 1986) results from oxidative doping, making the following activated electron transfer reaction possible:

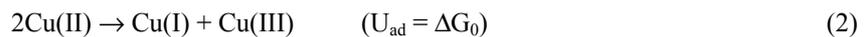


A part of the optical conductivity (Falck, Levy, Kastner, & Birgeneau, 1993; Kastner, Birgeneau, Shirane, & Endoh, 1998; Basov, & Timusk, 2005) is due to vertical excitation in the Marcus parabolooids, corresponding to Cu(II)/Cu(III) hole exchange.

The appearance of localized Cu(III) sites in the CuO₂ plane after doping was confirmed with the discovery of stripes (Tranquada, Sternlieb, Axe, Nakamura, & Uchida, 1995). In La_{2-x}Sr_xCuO₄ SC arises for x>0.05 due to interaction between the antiferromagnetic ground state and the charged state (Klimkans & Larsson, 2001; Larsson, 2010, 2012). The parallel CuO₂ planes are known to be responsible for SC. Spectra of different cuprates are similar, with a strong absorption covering a large part of the visible spectrum, including the ligand field transitions (Mott, 1968). We will mainly discuss optical conductivity spectra, and reflectivity spectra, particularly in the MIR region (Uchida et al., 1991; Falck, Levy, Kastner, & Birgeneau, 1993; Kastner, Birgeneau, Shirane, & Endoh, 1998; Basov, & Timusk, 2005).

Since Cu(III) sites require less energy to accept electrons than Cu(II) sites, intensity builds up in the region below 1.2 eV after doping (x>0), roughly proportional to the number of Cu(III) sites (Uchida et al., 1991). Spectral density at ≈2 eV is transferred down with an isosbestic point at ≈1.6 eV. The MIR peak is covered by the new absorption with an initial maximum at 0.5 eV. At higher doping levels the Drude peak builds up.

The pairs are created in a *disproportionation* reaction (or Hubbard-U transition (Uchida et al., 1991)) for which the free energy ΔG₀ is the *adiabatic* Hubbard U (U_{ad}):



Electron pair transfer (EPT) is exchange of the type:



with coupled vibrational motion. The obvious condition for SC, except that the atoms of the lattice must be the same, is that the activation energy for the reaction in Equation (3) should tend to zero, which in practical terms means delocalization. Pairing is spontaneous if the free energy ΔG₀=U_{ad}≤0. If the states which can be reached below a certain temperature correspond to an even number of electrons, the electrons are paired.

2. Charge Transfer Spectra

Copper(II) ions with water or oxygen ligands, such as Cu(H₂O)₆²⁺, or Cu(H₂O)₄²⁺ ions in water solution and the crystal CuSO₄·5H₂O are green-blue due to absorption in the red. The highest (singly) occupied orbital has Cu3d(x²-y²) symmetry and is strongly mixed with O2p. The blue colour is due to ligand field transitions.

The crystal water may be removed by heating. In CuSO₄ the ligand field transitions now appear in the infrared below the visible region, making CuSO₄ white. The reason for this may be the strong bonds in the SO₄²⁻ negative ions, making the oxygen bonds to the Cu²⁺ ion weaker, as compared to the bond between H₂O and Cu²⁺.

With crystal water CuCl₂ is green, but in pure form CuCl₂ and some other salts are brown like the cuprates and CuO, signalling strong absorption in the visible region. We argue here that the latter absorption in the visible region is due to MM (CuCu) transitions. Typical for MM charge transfer transitions is that their energy is high if the distance between the metal ions is large. If the distance is as small as about 3 Å, the absorption falls in the visible region. This applies to cuprates, CuO, CuCl₂, but not CuSO₄. In the latter case the distance between the copper(II) ions is considerably larger than for the first mentioned compounds, making the MM-transitions fall above the visible region.

It may be interesting to compare the Mott oxides CuO and NiO (Newman & Chrenko, 1959). In Ni(II) compounds the MM absorption is at a high energy, which is related to the instability of Ni(I). However, Cu(I) is stable due to a filled 3d-shell and the MM transitions are low.

On the other hand there is no reason to believe that the ligand-metal (LM) charge transfer transitions (O2p → Ni3d) are lower in CuO than in NiO. The LM transitions are above 4 eV in NiO. LM charge transfer energies are lower the higher the oxidation state of the metal ion. In MnO₄⁻, where Mn has the oxidation state +VII (with unoccupied d-orbitals), a strong LM-transition appears in the visible part of the spectrum. The same transitions exist in CrO₄²⁻, where Cr is in the oxidation state +VI, but are higher in energy and red-yellow. In TiO₂, where Ti has oxidation state IV, the LM absorptions appear in the UV region. In cuprates the valence state of copper is only II and the LM charge transfer energy therefore high, probably higher than 4 eV.

There is also no reason to believe that metal-ligand (ML) transitions are lower in Cu(II) than in Ni(II) compounds. 3d→4s transitions are in the ultraviolet (>3 eV) and forbidden, and the allowed 3d→4p transitions should be another 2 eV higher. In conclusion the LM and ML transitions in cuprates are higher in energy than the ligand field transitions and even the MM transitions.

Absorption around 2 eV in the cuprates is polarized only in the CuO₂ plane (Perkins et al., 1993; Falck, Levy, Kastner, & Birgeneau, 1992) as expected from MM transitions in the CuO₂ plane. LM and ML transitions are polarized in all directions. Hence the gap at 1.7-2.5 eV is due to MM transitions (Hubbard-U_{vert}).

Part of the misunderstanding regarding LM charge transfer spectra arises from a paper which shows the same satellite structure of La_{2-x}Sr_xCuO₄ and YBa₂Cu₃O_{6.7} as for other Cu²⁺ systems (Fujimori, Takayama-Muromachi, Uchida, & Okai, 1987). The result is correctly interpreted as due to a more attractive Cu site after 2p-ionization, according to the Sawatzky-Larsson model (Larsson, 1976). The Cu2p-hole is mainly screened by increased 3d-character in the occupied Cu3d-O2p molecular orbitals. The satellite/main line energy gap is equal to the LM energy gap, and it remains at about 4 eV after Cu2p ionization (Fujimori, Takayama-Muromachi, Uchida, & Okai, 1987). In any case Cu2p ionization is not involved in SC.

3. The Marcus Model for Cuprates

The bondlengths between the atoms at a site depends on the number of electrons present. To every local state belongs a set of bondlengths and bondangles. A Cu(III) site with empty Cu-3d(x²-y²)-O2p antibonding molecular orbital has a shorter (by about 0.1 Å) CuO bond than a Cu(II) site, which contains one electron in this orbital. A typical case is single electron exchange [Figure 1(a)]. The exchange rate varies depending on activation barrier. Activation barriers are large or small depending on bondlength differences. Vibrations, bondlengths and activation barriers are coupled.

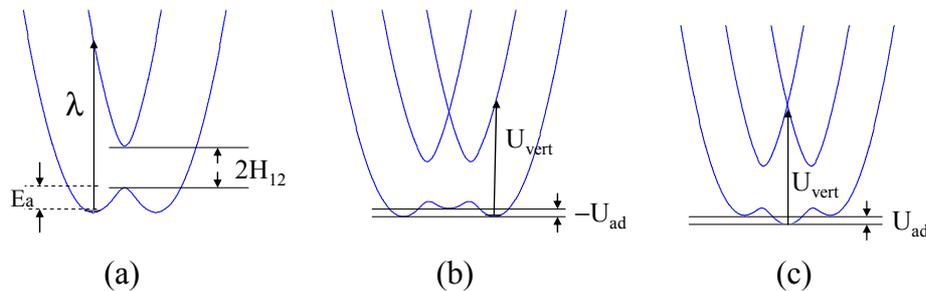
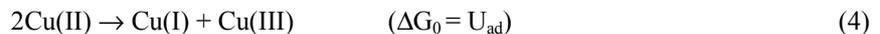


Figure 1. Potential energy surfaces in the Marcus model. (a) one-electron transfer; reorganization energy (λ), coupling ($2H_{12}$) and activation energy (E_a) are shown; (b,c) electron pair transfer. U_{vert} and U_{ad} are shown. (b) negative U case ($U_{ad} < 0$) and (c) positive U case ($U_{ad} > 0$)

Disproportionation energy is equivalent to adiabatic Hubbard U :



The vibrational breathing or half breathing mode is coupled to CuO bondlength, in its turn coupled to disproportionation, as indicated in Figure 1. Figure 1(b) is the spontaneous reaction with $U_{ad} < 0$, while Figure 1(c) shows the case typical for cuprates with $U_{ad} > 0$.

Heikes and Johnston were the first to make a systematic study (Heikes & Johnston, 1957) of the Mott insulators MnO, CoO, NiO, and CuO. Cu(III) sites were created by doping with Li₂O. The cuprates have a similar activated conductivity if slightly doped. Apparently localization occurs in cuprates as well as in CuO, and this is consistent with the existence of stripes (Tranquada, Sternlieb, Axe, Nakamura, & Uchida, 1995; Tranquada et al., 2004). Cuprates are polarons rather than semiconductors and have rich absorption spectrum in the “bandgap” (Perkins et al., 1993; Perkins, Birgeneau, Graybeal, Kastner, & Kleinberg, 1998). Oxidative doping of cuprates changes some Cu(II) to Cu(III) sites in the CuO₂ plane. Conductivity with the low activation energy of about 0.035 eV appears (Preyer et al., 1989), due to single electron exchange. The conductivity is

$$I \sim v_n \cdot \kappa \cdot \exp\left(-\frac{E_a}{k_B T}\right) \quad \text{where} \quad \kappa = \frac{\Delta^2}{4\pi\hbar} \left(\frac{\pi^3}{\lambda k_B T}\right)^{1/2} \quad (5)$$

E_a is the activation energy, κ the electronic transmission factor, and v_n the vibration frequency of the activating motion, λ is reorganization energy and Δ gap energy (Brunschwig, Logan, Newton, & Sutin, 1980). Equation (5)

has a peak in the conductivity, typical for hopping. The T-dependence of κ originates from the Landau-Zener avoided crossing problem (Landau, 1932).

The reorganization energy (λ) is also the vertical excitation energy from the $\text{Cu}^{2+}/\text{Cu}^{3+}$ to the $\text{Cu}^{3+}/\text{Cu}^{2+}$ energy surfaces (Figure 1a). This is very likely the origin of the 0.13 eV excitation measured by Falck, Levy, Kastner, and Birgeneau (1993) for $\text{La}_2\text{CuO}_{4+y}$. The thermal activation energy is only $\frac{1}{4}$ of the excitation energy in the Marcus model, or $\frac{1}{4} \cdot 0.13 \approx 0.033$ (Figure 1a).

Ono et al. have made a fitting to the Hall coefficient R_H (Ono, Komiya, & Ando, 2007; Timusk & Statt, 1999; Dzhumanov, Ganiev, & Djumanov, 2014; Hazra, Mandal, & Ghosh, 1996) of a similar type as in Equation (5), but with two activation energies: $E_a^{(1)} = 0.0435$ eV and $E_a^{(2)} = 0.445$ eV. According to the Marcus model the optical excitation energy is four times as much, i.e. $U_{\text{vert}}^{(1)} = 0.174$ eV and $U_{\text{vert}}^{(2)} = 1.78$ eV. We may interpret this as follows: The lower activation energy is due to Cu(II)/Cu(III) exchange and the higher to charge transfer of disproportionation type (Hubbard U_{vert}), followed by electron pair transfer

As a function of temperature (T) resistivity is infinite for $T=0$, goes through a minimum (T^*) and then increases as for a metal, for increasing T (Takagi et al., 1992; Hwang et al., 1994). If the system is superconducting for $T < T_C$, the resistivity in the CuO_2 plane quickly rises for $T > T_C$, goes through a maximum, and then drops to a minimum before it rises in the same way as for a metal. The resistivity ρ_{ab} thus shows a maximum between T_C and T^* .

A very small increase of doping level may decrease resistivity from infinity to zero, as $T \rightarrow 0$ (Takagi et al., 1992; Hwang et al., 1994). Above and below the critical level, the resistivity curves run parallel from large T down to T^* . Already at T^* the resistivity of the superconductor starts to deviate but is still close to the underdoped curve until a maximum. The minimum at T^* is considered to be due to opening of the pseudogap. Apparently there are two different mechanisms for conductivity. One has to do with activation of single electron hopping conductivity, tending to metallic above T^* . The other leads to a superconducting gap as $T \rightarrow 0$. We may conclude that the mechanism for SC is very different from the mechanism for metallic conductivity or electron hopping. The former is due to electron pair transfer (bosonic behaviour) and the latter to electron transfer [Cu(II)/Cu(III)] exchange (fermionic behaviour). Small energy differences determine the statistics.

In the Marcus model for *electron pairs* there are three energy surfaces of near parabolic shape. The ground state for cuprates is known to be a spin coupled, antiferromagnetic phase in the case of cuprates of type Cu(II)/Cu(II). Two higher states are charged states of the type Cu(I)/Cu(III) and Cu(III)/Cu(I). A major difference to the traditional Marcus case is that we need the Hubbard-U parameter for the difference in total free energy between charged state and the spin-coupled state.

The large width of the MM state follows from the fact that the final state is the strongly sloping site of the charged state parabola (Figure 1c). Electrochemical potentials for disproportionation reactions have been published for a number of systems as "Frost diagrams". More information and references can be found on Internet. Unfortunately Cu(III) is unstable in water solvent, and hence there may be scarce experimental data regarding the redox potential for the case of disproportionation of Cu(II).

We conclude from Figs. 1b and 1c that there are more than one way to define Hubbard-U: The vertical excitation energy, U_{vert} , and the adiabatic energy difference in the equilibrium points of the total energy parabolas, U_{ad} are different by nearly 2 eV.

In summary Marcus type models, particularly the Jortner version (Kestner, Logan, & Jortner, 1974; Jortner, 1976; Jortner & Bixon, 1969; Brunschwig, Logan, Newton, & Sutin, 1980), tells us which vibrations or phonons are coupled to electron pair transfer ("the electron-lattice polarization effect") (Takagi et al., 1992; Hwang et al., 1994; Moskvina, 2011). Since the Marcus parabolas are total energies, the change of curvature at curve crossings reveals itself in vibration spectra ("dynamic charge inhomogeneity") (Takagi et al., 1992; Hwang et al., 1994), and in time resolved spectra (non-linear lattice dynamics) (Moskvina, 2011). Since the weak dependence of T in κ can be ignored, Equation (5) shows that the dependence of T is essentially exponential. The Jortner model, on the other hand, uses vibronic energy levels for tunnelling of the nuclei through the activation barrier. For very low T there remains one level for tunnelling (Kestner, Logan, & Jortner, 1974; Jortner, 1976; Jortner & Bixon, 1969; Brunschwig, Logan, Newton, & Sutin, 1980), leading to slower decrease of rate.

4. Hubbard-U

In Mott's interpretation Hubbard U is excitation energy over a charge transfer transition from metal to the adjacent metal atom ((Kestner, Logan, & Jortner, 1974; Jortner, 1976; Jortner & Bixon, 1969; Brunschwig, Logan, Newton, & Sutin, 1980). However, the atomic integral *does not* approximate the charge transfer energy.

In semi-empirical quantum calculations, where ϕ is an approximation to an atomic orbital, the value of the integral in Equation (6) is 15 - 20 eV for transition metal ions or carbon atoms. Values in this range using atomic ab initio methods have been published for cuprates, but they are certainly meaningless. The energy of charge-transfer excitations have a number of negative contributions (Larsson, 2013).

$$U = \int \phi^*(1)\phi^*(1) \frac{1}{r_{12}} \phi(2)\phi(2) dV \quad (6)$$

If Equation (6) is adopted, obviously $U > 0$. Mott improved Hubbard-U by defining U as the difference between ionization energy I and electron affinity (Mott, 1968), not included in Equation (6):

$$U = I - A \quad (7)$$

Even with this definition $U > 0$ in most cases. By Equation (7) U is the energy for removing an electron from one site and putting it on another site, so far away that the attractive energy between the positive hole and negative electron can be neglected (Mott, 1968). The intention of Mott was obviously to obtain a simple measure of the charge transfer energy in an oxide or salt. It is unclear why he did not want to include the electron-hole attraction, which is simply $1/R$ Hartree (atomic units), if the distance between hole and electron after charge transfer is R Bohr = $R \cdot 1.89 \text{ \AA}$. Since the electron-hole interaction is in fact large, the electron avoids transferring a long distance in an actual experiment (for example in a solid state charge transfer transition, in a photosynthetic charge separation or in the creation of static electricity). If the distance between the hole and the electron is R , one at least has to improve Equation (7) to the acceptable definition:

$$U_{ad} = I - A - 1/R \quad (\text{atomic units}) \quad (8)$$

$R \rightarrow \infty$ is unrealistic. There are additional corrections to Equation (8), however. In fact U has to be understood as a free energy, and then the only possible equation is

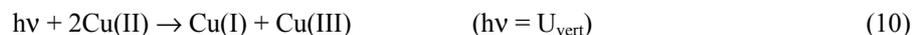
$$U_{ad} = \text{DPE (disproportionation energy)} \quad (9)$$

DPE can be obtained from electrochemical data in fortunate cases. Seldom U_{ad} exceeds a fraction of an eV, and is frequently negative. Obviously $U_{ad} < 0$ for a "missing" valence state such as Tl^{2+} , which disproportionates into Tl^+ and Tl^{3+} , contradicting eqs.(6,7). Generally the negative "lattice enthalpy" has to be added (Larsson, 2013), since there is always attraction between the positive hole and the negative electron (Born, 1919; Haber, 1919).

Doping introduces attractive Cu(III) sites, making U_{ad} negative and the charged phase eventually stable (Larsson, 2013). SC occurs in the interphase (Larsson, 2012, 2013) between charged and spin coupled phase.

5. Assignments in Visible and IR Spectra

The large gap below 1.7 eV in pure cuprates (Larsson, 2013) is easy to explain in a local picture, since the only possibility for electronic states are ligand field states and MM charge transfer states. Both start above 1.7 eV, but only the latter are allowed. For historical reasons the MM-transitions are called Mott-Hubbard states (Mott, 1968). The strong absorption is thus due to electron transfer $a \rightarrow b$ between adjacent sites A and B with equal valence:



The energy is increasing with transfer distance, but the transition moment is decreasing. a and b are $Cu3d(x^2-y^2)$ orbitals (same spin and strong ligand admixtures) on adjacent sites A and B, respectively. Tokura et al. compared optical conductivity in a number of cuprates (Tokura et al., 1990), and tried to correlate peak maximum at 1.5 - 2 eV with structure. The reason for the quite large width is obvious from the Marcus model. The energy of the charge transfer state is parabolic, but with equilibrium distance different from the one of the ground state. It follows that the energy of the final state is strongly sloping (Figures 1, 2). The large width is thus due to the (half)-breathing vibrations of the Marcus model.

There are two nearly parabolic energy surfaces with different equilibrium points, corresponding to spin-coupled ($ab+ba$) and charged aa , bb , forming a spin-coupled ground state and excited charged states, respectively. The created Cu(I)/Cu(III) pair relaxes its geometry along the left parabola of Figure 2. After doping there are Cu(III) sites which may be regarded as deeper holes for the electrons.

Perkins et al. studied optical absorption in several undoped cuprates ($x=0$) with all copper atoms in the valence state II, and found weak absorption in the MIR region with polarization in the CuO_2 plane (Perkins et al., 1993). The sidebands have been interpreted in different ways. Here a different interpretation is suggested, where the weak absorption is due to vibrational excitation that obtains intensity due to the influence of the charge transfer

state on the ground state energy surface (Figure 2). Below the avoided crossing the vibrational levels of the charged state perturb slightly the vibrational levels of the ground state, making the transition slightly allowed.

The transition moment for x-polarized light is:

$$\mu_x(Q) = \langle \phi_i | x | \phi_a \rangle \cdot \langle \Xi_{iv} | \Xi_{au} \rangle \quad (11)$$

In the present case the orbitals ϕ_i and ϕ_a are $3d(x^2-y^2)$ molecular orbitals at adjacent sites. They overlap through the oxygen $2p_x$ or $2p_y$ orbitals. μ_x and μ_y , but not μ_z , are different from zero for orbitals in the CuO_2 plane. The vibrational levels and the electronic levels together forming vibronic levels, and borrowing intensity from the other, higher parabola, thereby making some higher vibrational levels weakly allowed.

In Equation (11) $\langle \Xi_{iv} | \Xi_{au} \rangle$ is the vibrational overlap between vibrational states v and u belonging to the i and a electronic states, respectively. Since these states belong to different electronic states the overlaps occur particularly in the region where the two parabolas in Figure 2 are intersecting. Very likely this is the reason for the non-zero intensity for the MIR transitions, and explains the correlation between the MIR absorptions at 0.4 and the absorption at 1.7 eV. The MIR absorption is of MM-type and the electronic interaction between the energy curves is due to electronic overlap via oxygen $\text{O}2p$.

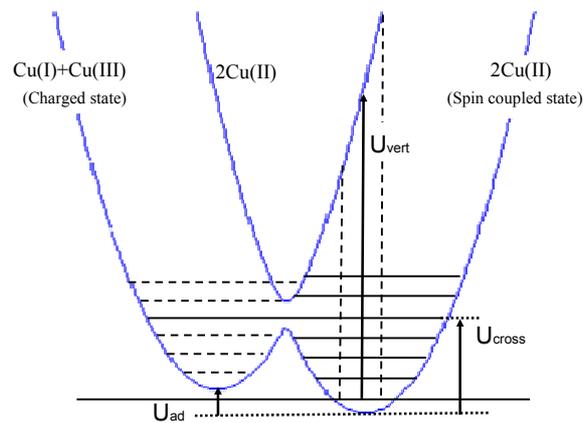


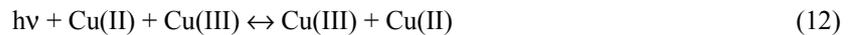
Figure 2. Marcus model for electron pairs. Dashed vertical lines demonstrate the width of the absorption at ≈ 2 eV. Full lines: Vibronic levels. Perturbing vibrational levels of the charged state are dashed

Uchida et al. (1991) demonstrated transfer of spectral density to lower energies after doping, as already mentioned. Absorption increases fast with doping in the whole region below 1 eV. For 6%, as compared to 2% doping, Uchida et al. (1991) find a further move of the spectral density to even lower energies, ending up in the Drude peak.

How are we going to explain that spectral density, polarized in the CuO_2 plane, upon doping is moved from the large absorption peak at ≈ 1.7 eV to the region below 1.5 eV, and most of it below 1 eV (Uchida et al., 1991)? Both the strong absorption around 2 eV and the weaker one below 1.5 eV are polarized in the CuO_2 plane, and this together with high intensity shows that we are dealing with MM charge transfer transitions. The ligand field transitions whose intensity can be neglected compared to the MM transitions, may be one reason for the less than perfect isosbestic point.

The transfer of spectral density is not restricted to cuprates. Katsufuji, Okimoto, and Tokura (1995) show that varying x from 0 to 1 in $\text{R}_{1-x}\text{Ca}_x\text{TiO}_3$, where $R = \text{La}, \text{Nd}, \text{Sm}, \text{or } \text{Y}$, moves spectral density from the region above 1 eV to the region below 1 eV. For $x=0$ there are only Ti(III) sites (one 3d electron per Ti); for $x=1$ (CaTiO_3), only Ti(IV) sites with no Ti3d electrons. If there are only Ti(III) sites, disproportionation to Ti(II)/Ti(IV) is possible at excitation, with Hubbard $U_{\text{vert}} \approx 2$ eV. After Ti(IV) sites have appeared for $x>0$, vertical electron exchange reactions at a low energy become possible (Figure 1a), but Ti(II) sites start to disappear. Weak absorptions below the MM transition energy (U_{vert}) are quite common in transition metal oxides after doping, and indicate a possibility for SC. Whether or not SC appears is controlled by Hubbard- U_{ad} .

Thus when Cu(III) sites become available in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x > 0$) there are many new possibilities for photo-induced charge transfer, for example of the type:



This is *one* reason for transfer of spectral density to the lower energy range.

Also transitions of the form seen in Equation (10) are possible at a lower energy, and these are connected to the pseudogap. The pseudogap has been discussed in earlier publications (Larsson, 2010, 2012). The active orbitals are $\text{Cu}3d(x^2-y^2)$ mixed with $\text{O}2p(x)$ and $\text{O}2p(y)$. If this orbital is called a on site A and b on site B, the hole state is $ab+ba$ and forms the spin-coupled ground state of undoped cuprates. The hole states aa and bb are the charged states. The ground state is a superposition of $ab+ba$ and $aa+bb$. Without doping the $aa+bb$ state is 1.7 - 2.5 eV vertically above the ground state $ab+ba$, but only ≈ 0.2 eV in an adiabatic process. The activation energy for creating $aa+bb$ and $aa-bb$ in a thermal process should be $\approx 1/4 \cdot 2$ eV in the Marcus model, if U_{ad} is neglected.

The pseudogap is due to the transition $ab+ba \rightarrow aa-bb$ (Larsson, 2010). In the superconducting region, the mixing of $ab+ba$ and $aa+bb$ forms the ground state and the superconducting gap to $aa-bb$. With less doping this gap becomes the pseudogap and can no support SC because of the term $ab+ba$ (Larsson, 2010, 2012). The pseudogap is lower in energy but becomes increasingly visible as the number of charges in the CuO_2 plane is increased. The charged energy curve in the Marcus model, Figs. 1b,c and Figure 2, lower its energy compared to the spin-coupled state (Larsson, 2012), due to the increased number of Cu(III) sites.

6. Discussion

Cuprates are different from other copper compounds by the existence of square planar CuO_2 planes where the number of electrons per site can be changed by doping. This makes three phases possible, a charged phase, an antiferromagnetic phase and a superconducting phase (Larsson, 2012). The former two are insulating, but may interact and form a superconducting phase (Larsson, 1986; Basov, & Timusk, 2005). The ground state without doping is the anti-ferromagnetically ordered phase. With slight oxidative doping Cu(III) sites appear among the Cu(II) sites. New quantum mechanical states appear, of the following type:

1). The local Cu(III) site can interact with Cu(II) sites by electron exchange at the same or slightly different energy. For each pair of Cu(III)/Cu(II) sites there is now another electronic state of the type Cu(II)/Cu(III). To this new situation the Marcus model is a very useful model, which is complementary to ligand field theory for single sites.

In a localized mixed-valence system it is legitimate to use a localized theory and use concepts such as charge transfer states and charge transfer gap. The Cu(II)/Cu(III) interaction puts its marks on the absorption and photoconductivity spectra, and is very likely responsible for the absorption at 0.13 eV.

2). The pseudogap is the gap formed between an inter-site two-electron state due to interaction between the hole states $ab+ba$ and $aa+bb$ and the $aa-bb$ excited state. For decreasing Hubbard U , the $aa+bb$ component in the ground state is increased compared to the $ab+ba$ component. The ground state tends to $aa+bb$ when U_{ad} turns negative and the gap is then to $aa-bb$. Only paired states are now present at low energy and the system may become superconducting and follow Bose-Einstein statistics.

3). Vibrational levels which borrow intensity from charged states. In the “final” interactions a superconducting phase with a vibronic ground state is formed with concerted motion of electrons and nuclei, in a similar way as in the Cooper model (Cooper, 1956).

The vertical gap, U_{vert} , is ≈ 2 eV and the adiabatic gap, U_{ad} , only ≈ 0.2 eV. This may be considered anomalous compared to the corresponding values for NiO, and depends on the fact that copper has three stable oxidation states Cu(I), Cu(II), and Cu(III).

At oxidative doping of the pure cuprate the absorption at 2 eV is decreased. The reason is simply that the average energy needed to move the electron to the other site is decreased with an increased number of Cu(III) sites. The maximum value is ≈ 2 eV without doping, *since all other sites are Cu(II) sites*. When holes are created, so that the Cu(III) sites are formed, the energy spectrum is completely changed. It is possible to excite into the hole or to sites adjacent to the holes.

Hubbard- U is a free energy and has to be calculated as a free energy. The only existing, accurate calculation (as far as I know) has lead to a value of U_{ad} close to zero (Klimkans, 2001). The most common shortcoming is that the cluster has been too small (sometimes just the copper ions), that correlation effects have not been included, or that Coulomb fields have not been included properly.

The assignment of spectra given here shows the importance of structural differences between different oxidation states. This structural dependence is also of decisive importance in the nuclear dynamics of excited states and electron transfer (Reznik et al., 2006; Mankowsky et al., 2014). These problems will be discussed in forthcoming publications.

7. Conclusion

SC depends on electron pairing on Cu sites and successive, activationless electron pair transfer between the sites. It develops in a localized system under the conditions that make $U \rightarrow 0$. Hole-doped cuprates are good examples that doping tends to make the Cu^+/Cu^{3+} charged phase more stable and hence make $U \rightarrow 0$ (Larsson, 2013). Configuration interaction between the insulating charged and spin-coupled configurations leads to a superconducting state.

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