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## Energetics and ordering in strongly correlated oxides as seen in optics

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*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

2003

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Presura, C. (2003). *Energetics and ordering in strongly correlated oxides as seen in optics*. s.n.

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# Chapter 1

## Introduction

### 1.1 General Introduction

Transition metal oxides are compounds formed from oxygen and transition metals elements existing in the middle of the periodic table (Cu, V, Cr, etc.). Some of them have been used since ancient times as pigments, because they may present strong optical absorptions, which lead to color. Besides this, they exhibit a large variety of physical properties. They can be metals ( $\text{CrO}_2$ ), semiconductors ( $\text{Cu}_2\text{O}$ ) or large gap insulators ( $\text{V}_2\text{O}_5$ ). Magnetically, they can behave as ferromagnets ( $\text{CrO}_2$ ), ferrimagnets ( $\gamma\text{-Fe}_2\text{O}_3$ ), or antiferromagnets ( $\alpha\text{-Fe}_2\text{O}_3$ ). They could attain even superconductivity at relatively high temperatures ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ).

A common characteristic of the most transition metal oxides is the small radial extent of the valence 3d orbitals, which is comparable with the interatomic distance, and thus the valence electrons may form narrow bands, or they could experience strong Coulomb interactions, leading to correlated motion. It is important to remember here that, in principal, Coulomb repulsion forces exist in any crystal, but do not lead immediately to a correlated electron motion. For example, the usual metals may be seen as a collection of non-interacting renormalized electrons. The reason is that the kinetic energy of the electrons, in a high density electron gas, is much larger than the interaction one.

In the transition metal oxides, the small radial extent of the valence 3d orbitals leads mainly to a strong on-site Coulomb repulsion. Here, the motion of electrons on some sites is strongly influenced by the partial presence of other electrons on those sites, and thus the motion may be correlated. This type of correlation is best exemplified by the antiferromagnetic materials, where the spin of two neighboring electrons orient in opposite direction, not because of the direct magnetic field produced by the spins, but because in this situation they can virtually hop between the two sites. We call a system *strongly correlated*, if taking into account this Coulomb interaction is essential in understanding the main physical properties.

Because the electrons in the transition metal oxides are highly correlated, a complicated relationship between the electronic, spin and lattice degrees of freedom may set in. Thus, the atomic character may be in competition with the itinerant character. In some cases, this may lead to exotic magnetic properties, since the localized character favor the local magnetic moment according to the Hund's rule, and the band character favors the

Pauli paramagnetism. Under specific conditions, the interplay of these degrees of freedom results in an equilibrium, where we can find regular patterns across the transition metal sites in the sample. Charge or spin ordering of the ground state may be easily found in many compounds. In addition, an ordering of the orbitals on which valence electrons reside may appear. This is proposed for example as the possible mechanism responsible for the temperature-induced magnetization reversal in  $\text{YVO}_3$  [1].

If both localized and itinerant carriers exist in the material, coupling between them may arise. For example, strong coupling between correlated itinerant electrons and localized spins, both of 3d character, arises in  $\text{R}_{1-x}\text{X}_x\text{MnO}_3$  (where  $\text{R} = \text{La, Pr, Nd}$ ;  $\text{X} = \text{Sr, Ca, Ba, Pb}$ ) compounds. This leads to giant magnetoresistance effects (a huge change of the resistance when the magnetic field is applied, such as four orders of magnitude change in thin films of  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [2]).

Many properties of the transition metal oxides can be fine-tuned with chemical substitution. The best examples of how sensitive the properties may be to chemical composition are the high temperature superconductors [3]. Here, a change of stoichiometry in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  from  $\delta = 0$  to  $\delta = 0.16$  turns an antiferromagnetic insulator into a superconductor.

Another property of many transition metal oxides is low dimensionality. Even though the interactions are clearly three-dimensional (the atoms stick together to form a three-dimensional crystal), the main physical properties may be considered as coming from electrons interacting only inside some planes (two dimension 2D) or lines (one dimension 1D). Examples of 2D materials are the high temperature superconductors [3], ladder compounds such as the  $\alpha$  phase of the pentoxides [4], or triangular Kagomé lattices where geometric magnetic frustrations may occur [5]. As 1D system we may cite here the inorganic spin-Peierls material  $\text{CuGeO}_3$  [6].

Low dimensionality creates also sensitivity when different parameters are changed. For example, in low-dimensional spin systems, quantum fluctuations could result in qualitatively different low-energy behavior. Haldane conjectured [7] that antiferromagnetic spin chains with integer spin would have a gap in the energy spectrum, whereas the spectrum of chains with half integer spins is gapless.

Many other examples of exotic properties of transition oxide materials may be enumerated here. However, we will concentrate next on the two classes of low dimensional oxides studied in this thesis: vanadium pentoxides doped with sodium (Chapters 3 and 4) and high temperature superconductors (Chapter 5). Both materials were studied experimentally using optical spectroscopy. An introduction to one of the spectroscopic techniques used, namely ellipsometry, is presented in Chapter 2.

## 1.2 Vanadium Pentoxides

Vanadium pentoxides represent an interesting class of transition metal oxides whose properties may be easily changed by chemical composition. This class is given by the parent insulating compound  $\text{V}_2\text{O}_5$  [4]. The structure of  $\text{V}_2\text{O}_5$  consists of layers of square pyramids of oxygen atoms surrounding a  $\text{V}^{+5}$  ion and thus, on pure chemical grounds, V has no valence 3d electrons. Here, many new vanadium pentoxides can be formed by

adding different electronic donors ( $A=\text{Li, Na, Ca, Mg, etc.}$ ). The  $A$  atoms enter the space between the layers and act as electron donors for the  $\text{V}_2\text{O}_5$  layers, creating three possible phases,  $\alpha$ ,  $\beta$ ,  $\gamma$  [4].

Our results on the  $\alpha$  phase of some vanadium pentoxides doped with sodium, namely  $\alpha'$ - $\text{NaV}_2\text{O}_5$ ,  $\alpha'$ - $\text{Na}_{1-x}\text{Ca}_x\text{V}_2\text{O}_5$  ( $0 \leq x \leq 0.2$ ) and  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  ( $0.85 \leq x \leq 1.00$ ) are presented in Chapter 3. Doping  $\text{V}_2\text{O}_5$  with a lower concentration of  $\text{Na}$  atoms, such as in  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ , creates the second  $\beta$  phase. Our results on the measurements on this  $\beta$  phase are presented in Chapter 4.

The  $\alpha$  phase form a two-dimensional ladder pattern of  $\text{V}$  atoms. Its best known representant is  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , in particular because at  $T_c=35\text{K}$  a phase transition occurs, below which two changes take place simultaneously [6]: a doubling of the unit cell along the ladder direction and an opening of a spin gap. At the time of its discovery it was wrongly suspected (because of a previous wrong determination of a crystal structure [8–10]) that the material presents a spin-Peierls transition (a transition where two by two electron spins of neighboring  $\text{V}$  atoms pair to form a singlet). This would have made  $\alpha'$ - $\text{NaV}_2\text{O}_5$  the second inorganic material having a spin-Peierls transition after  $\text{CuGeO}_3$  [6]. However, later measurements regard the material rather as a charge order system [11].

The mechanism of the phase transition, the main focus of research on  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , is at this point not explained, even though several proposals exist [11, 12]. The system is generally seen as a quarter-filled ladder compound with the spins carried by  $\text{V-O-V}$  molecular orbitals on the rungs of a ladder [10], and strong on-site Coulomb repulsion (thus, it is a strongly correlated electron system). The  $\text{V-O-V}$  unit behaves mainly as a  $\text{H}_2^+$  molecule, with the ground state in a bonding state and the first excited state in an antibonding configuration. A peak would then evolve in the optical spectra corresponding to the bonding-antibonding transition of the on rung molecular orbitals. This peak was detected in measurements [13]. Later, however, other explanations were also proposed for the peak, including an on-site d-d transition between the crystal field split levels of the  $\text{V}$ -ions[14].

To discriminate between these possibilities, we conjectured that by doping  $\alpha'$ - $\text{NaV}_2\text{O}_5$  with extra electrons, the intensity of the peak would show different behaviors. The electron doping is chemically realized in the single crystals samples of  $\alpha'$ - $\text{Na}_{1-x}\text{Ca}_x\text{V}_2\text{O}_5$ . These samples have been measured, and the results are presented and interpreted in the first part of Chapter 3. In addition, other temperature and doping dependencies of the vanadium pentoxides were measured, such as for  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$ . We present the results of these as well, in the second part of Chapter 3.

In chapter 4, some measurements on the  $\beta$  phase of the vanadium pentoxides are presented, namely for  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  [15, 16]. This material is one-dimensional: the resistivity along the chain direction  $b$  is two order of magnitude smaller that the one perpendicular to the chains.

The interest in this material arose recently, because better grown stoichiometric samples show additional phase transitions missed by the older samples [17]. Below room temperature, the system undergoes three phase transitions: a structural phase transition which doubles the unit cell at  $T_{\text{Na}} \simeq 240 \text{ K}$ , a metal-insulator transition at  $T_{\text{MI}} = 136 \text{ K}$  (accompanied by a tripling of the unit cell along the  $b$  axis[18]) and a magnetic transition at  $T_{\text{CAF}} = 22 \text{ K}$  [19, 20]. In addition, a transition into a superconducting state was

observed under high pressure[21].

These transitions, and the main electronic properties are not understood. Because the dilution of the donor electrons is high (one donated electron per 6 vanadium sites), the charge carriers are expected to acquire a polaronic character, in the sense that the movement of electrons disturbs the nuclei in their vicinity [22]. Strong electron-phonon coupling in  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  was earlier supposed to lead to formation of bipolarons [23].

The high dilution of the electrons donated to the V sites could also result in an almost equal redistribution of electrons on the three different V sites present at room temperature. This, in principle, would explain very naturally the tripling of the unit cell at the metal-insulator transition (remember that we have one donated electron per six sites). However, as pointed by Yamada in Ref. [17], the long range magnetic transition present in the system at  $T_{CAF} = 22$  requires that the donated electrons are close to one another, and capable of interacting magnetically. This is surprising, since the dilution is high, and hence the distance between donated electrons is large (one should not compare this is with the situation in the high temperature oxides, since there the doped charge carriers go into an antiferromagnetic background, but in  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  they go on an "empty" lattice with no other  $d$  electrons present).

To give an answer to this type of considerations, more experimental data are needed. Optical measurements on  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  are scarce in literature, and they are almost completely absent for the new grown samples. That is why we considered that measurements in infrared and visible range could settle many important issues in this compound. In the Chapter 4 we present the results of our endeavor.

### 1.3 High temperature superconductors

The exotic properties of the oxides are probably best exemplified by the high temperature superconductors, which is the subject of chapter 5. These are layered structures of  $\text{CuO}_2$  square patterns, interleaved by various cations layers which provide different doping to the  $\text{CuO}_2$  planes. They are also generally named cuprates, even though high temperature superconductors without Cu have been found. If no doping is present, then the copper atom is in the  $\text{Cu}^{+2}$  configuration, having a hole ( $d^9$  configuration) with a spin of  $1/2$  on every Cu site. The system is then a Mott insulator, in the sense that a strong on-site Coulomb repulsion localizes the electron wave function, and the system does not conduct. Moreover, due to a super-exchange interaction between the Cu spins via the O atoms, the ground state of these undoped cuprates is antiferromagnetic.

There are two types of dopings which can be induced in the  $\text{CuO}_2$  planes (by changing the concentration of cations, for example), electron and hole doping. The resulting phase diagram is presented in Fig. 1.1. As we can see, by doping, the Neél temperature ( $T_N$ ) for the antiferromagnetic-paramagnetic transition decreases. The reason why this decrease is faster in the hole doped regime, has to do with how the doping affects the magnetic interaction. In the hole doped regime, holes enter into the oxygen p-orbital in the  $\text{CuO}_2$  planes. This induces ferromagnetic coupling between the  $\text{Cu}^{+2}$  ions adjacent to the partially empty oxygen orbital. As a result, significant spin frustrations develop in the antiferromagnetic background, and a rapid decline of the Neél state is observed. On

the other hand, electron doping acts on the  $\text{Cu}^{+2}$  ions, giving rise to spinless  $\text{Cu}^+$  ions, that dilute the antiferromagnetic background, but do not introduce strong spin frustrations, and hence the Neél state survives over a broader range of electron doping, as is schematically drawn in Fig. 1.1.

Upon further doping of carriers, long-range antiferromagnetism vanishes, and superconductivity sets in. This came in the beginning as a surprise, since the parent undoped compounds are insulators, in contrast to the "classical" superconductors, which are metals. More important however, is the high temperature of superconducting transition attained by the cuprates. This reaches as high as 134K at ambient pressure (and 164K with a pressure of 30GPa) in Hg- based system  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ . The transition temperature  $T_c$  for all hole-doped cuprates varies almost universally with the carrier concentration per Cu ion as  $T_c = T_c^{max}[1 - 82.6(p - p_0)^2]$ , where the maximum transition temperature  $T_c^{max}$  is obtained for  $p = p_0 \sim 0.16$ . The two doping regimes below and above  $p_0$  are called underdoped and overdoped, respectively.

The high transition temperature of the hole doped superconducting cuprates has been the driving force behind a huge theoretical and experimental research on these compounds. An understanding of the basic mechanism leading to it is however still missing, unlike the case of classical superconductors, which are described remarkably well within the framework of BCS theory. This came both as a disappointment and as a challenge to the researchers in the field. The present situation looks like a game of puzzle, of which some of the lost puzzle pieces are recovered, but even assembled in some way, they still do not give the correct image. What is known, and what are generally accepted as the principal marks of the cuprates? We will try to summarize a small part of the immense knowledge accumulated over the past years.

A good understanding of the physics involved in the high temperature superconductors requires a correct identification of the basic building blocks, and a theory which binds these blocks together. BCS theory appeared in the beginning as a theory which, modified, may explain some of the physical properties of the superconducting cuprates. The usual ac Josephson effect frequency  $2eV/h$  was still observed [24], and thus Cooper pairs may be still formed. The observed flux quantum was also found to be of the usual magnitude  $hc/2e$ [25].

However, the basic building blocks of the BCS theory, the quasi-particles of the Fermi-liquid approach, were difficult to find in the normal state. This can be deduced from ARPES studies of the single particle spectral function [26], or indirectly from the analysis of different response functions of the system (such as spin or current) [27] and heat transfer [28]. Photoemission data at momentum  $(0, \pi)$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  have revealed that quasi-particles may exist in the superconducting state, but they disappear slightly above  $T_c$  [29]. In addition, the optimally doped samples show the in-plane resistivity which decreases linearly as the temperature decreases, as opposite to the quadratic behavior predicted by the Fermi-liquid theory (though generally accepted, this observation is still doubted by some researchers, see [30]).

As a result, most researchers would disregard Fermi-liquid approach as applicable in the normal state, even though at asymptotically low temperature and energies the physics may be dominated by quasi-particles [31]. This is not completely surprising, since the cuprates are characterized by strong repulsion between electrons, and it does also not

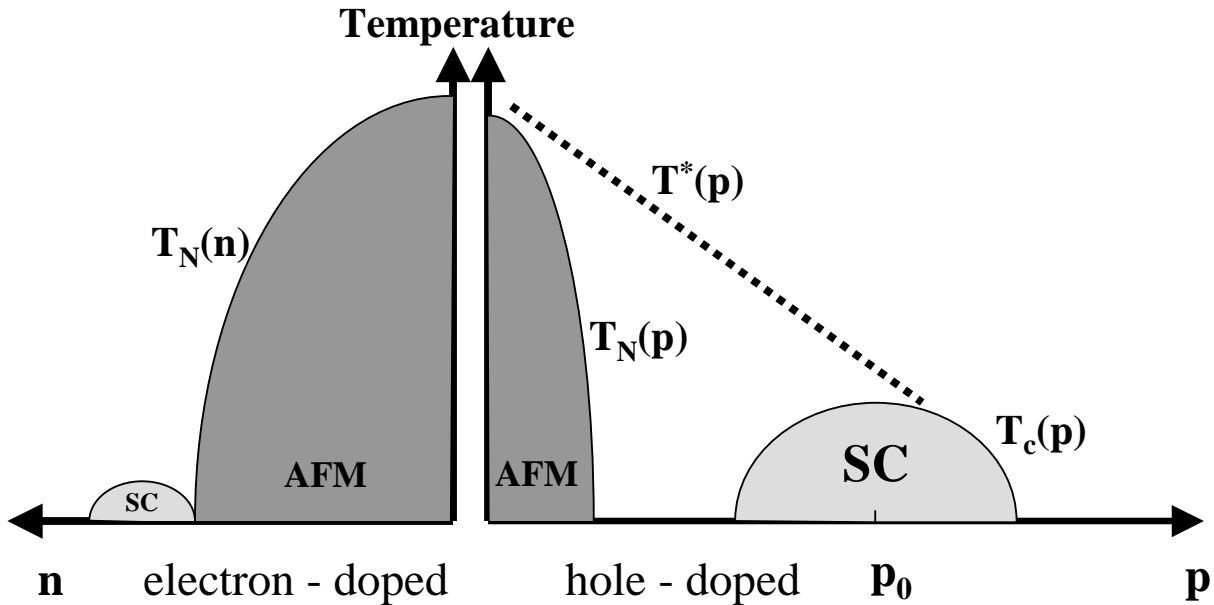


Figure 1.1: Generic phase diagram of the p-type and n-type cuprates. AFM designates the antiferromagnetic state, SC the superconducting state, and  $T_N$ ,  $T_c$ ,  $T^*$  are the Neel, superconducting and pseudogap transition temperatures, respectively.

completely disprove the BCS pair approach, but it led to the idea that maybe the pairing is different, for example a collective phenomenon [31].

The "glue" which binds the pair is another important ingredient to be found. In the classical superconductors, the "glue" is generated by the electron-phonon interaction. This explained why the transition temperature was so low, of the order of few or tens of K (the hierarchy gives  $E_F \gg \hbar\omega_D \gg k_B T_c$ ). This is also the main reason why the phonon interaction is disregarded as the interaction responsible for the high transition temperature in the cuprates, even though electron-phonon influence was observed (see for example the ARPES data from Ref. [32]).

Some remaining candidates for the "glue" are the electrons themselves. For example, a 'triplet' state, which was found to give an excitation at around 41 meV in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$  [33], was proposed to act as a binding agent [34]. Magnetically mediated superconductivity by quanta of the magnetic fluctuations was also observed in  $\text{UPd}_2\text{Al}_3$  [35, 36]. This may come as a surprise, since magnetism and superconductivity look like oil and water, the Meissner effect assuring that the superconductor will expel the magnetic field passing through it. However, the pairing may be given by the spin fluctuations, as suggested by the recent discovery of a superconducting phase inside a ferromagnetic phase in  $\text{UGe}_2$  [37].

More is known about the symmetry of the pair state. This has been long suspected to have a d-wave symmetry [38] (the order parameter changes sign under  $90^\circ$  rotation). By ingeniously designing tri-crystal substrates of  $\text{SrTiO}_3$ , and rendering the surface with a scanning SQUID microscope, Kirtley and coworkers [39] have been able to confirm the d-wave symmetry of the order parameter, giving thus a big blow to the phonon coupling schemes, which would result in the s-symmetry of the order parameter. This type of

symmetry agrees also with the highly anisotropic form of the superconducting gap  $\Delta(\mathbf{k})$  [40].

Because the parent undoped cuprates are Mott insulators, the Hubbard on-site Coulomb repulsion physics is expected to play an important role. As a result, many numerical computational procedures were dedicated to the problem. One of the first results to come out was the prediction of the so-called stripe order [41]. In the ground state, this consists of antiferromagnetic domains separated by domain walls on which the charge carriers reside. They could be in a static phase, or they could fluctuate. Their presence could explain very elegantly the position of the incommensurate magnetic peaks observed in neutron scattering measurements [42], as a function of the doping level. Later, more conclusive evidence for their presence was found [43, 44] in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Whether superconductivity originates in charge stripes is still a matter of debate, with arguments pro [44] and against.

The high temperature superconductors are not only characterized by a low carrier concentration ( $p_0 \sim 0.16$  yields about  $10^{21}\text{cm}^{-3}$ ), but also by a short coherence length, on the order of 2 or 3 lattice constants. This suggested that two "doped holes" in close proximity could form two-particle bound states, Cooper pairs, which would exist also in normal state [45], and then Bose-Einstein condense below  $T_c$ . This type of real space pairs was also dismissed (see for example the Ref. [31]), because then the chemical potential is expected to lie below the bottom of the band, whereas experimentally it is found to lie in the middle of the band.

Much attention was devoted over the time to the opening of the so-called "pseudogap", which appears in the underdoped and slightly doped samples below a temperature denoted by  $T^*$  in Fig. 1.1. The presence of the pseudogap manifests itself directly in infrared optical conductivity [46], or by plotting the frequency dependent scattering rate  $1/\tau^*(\omega)$  [47], as a small spectral weight at low frequencies. Its evolution may be a sign of the collective physics associated with the growth of the electronic correlations. One option presented in Ref. [31], is that as the temperature is lowered, the antiferromagnetic fluctuations develop, and since the antiferromagnetic excitations have a gap, one might expect that these fluctuations would contribute to the pseudogap as well. It was also argued that the superconducting gap would emerge from the normal state pseudogap, which would have a d-wave symmetry as well [48]. A generally accepted picture of the origin of the pseudogap is however missing.

To account for the observed experimental facts, many proposals have been put forward. P.W. Anderson proposed in the beginning the interlayer tunnelling mechanism [3, 49], where superconductivity arises from tunnelling of electron pairs between the copper oxide planes. Later, however, Moler [50] and Tsvetkov [51] have disproved this theory by measuring the c-axis penetration depth and the interlayer plasma frequency of electron pair oscillations. They showed that interlayer tunnelling mechanism provides only 1% of the condensation energy in  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ .

A different approach was also invoked, a so-called Resonance Valence Bond (RVB) state [52], a quantum ground state of the electronic system, which may play a decisive role. This follows the belief that the Hubbard models, or simplified  $t$ - $J$  models, lead to correlation effects which may play the leading role [53]. A important consequence of this theory is the spin-charge separation [54], in which low energy excitations consist of spinons



(no charge) and holons(no spin). However, no direct evidence for spin-charge separation has been obtained [55].

A phenomenological approach was used in creating the SO(5) theory [56]. It uses the fact that the HTSC emerges upon doping from the antiferromagnetic compounds. In the same way as a unification is usually done in the particle physics theories, SO(5) theory tries to unite the superconducting and antiferromagnetic phases in a larger symmetry group.

The superconducting state was also supposed to appear because frustrated kinetic energy of single charge carriers may be recovered when pairs are formed [57–59]. A model based on a kinetic energy driven mechanism of superconductivity may not require subtle induced attractions, since it may derive directly from a strong repulsion between electrons [31], but it would still require certain conditions, since a limited class of strongly correlated systems presents superconductivity. The same reduction of kinetic energy was invoked by Hirsch, who proposed a model in which the kinetic energy reduces when two holes come closer[60]. However, only recently, plausible experimental evidence was presented to support these scenarios, namely the optical measurements performed in the visible range for  $Bi_2Sr_2CaCu_2O_{8+\delta}$  [61, 62], which showed that indeed the kinetic energy lowers in the superconducting state.

The behavior of the other part of the electron energy, namely the Coulomb correlation energy, is not known. Leggett [63] has proposed that this energy would decrease in the superconducting state, as a result of the improved screening due to Cooper pair formation. He also proposed that the saving of the Coulomb energy would take place primarily at midinfrared frequencies (0.1-2 eV) and small momentum vectors  $q \leq 0.3\text{\AA}^{-1}$ . Some attempts have been done to measure these changes using Electron Energy Loss Spectroscopy, but they proved unsuccessful, due to resolution problems of the technique.

Optical spectroscopy does have the necessary resolution, but it probes the response of the system at much smaller momenta (given by the frequency of the light used). However, it may provide useful indications. With these thought in mind, we endeavored ourselves to measure carefully the temperature dependence of the optical properties for the underdoped and optimally doped  $Bi_2Sr_2CaCu_2O_{8+\delta}$ , and interpret the data in terms of the Coulomb energy stored in the center of the Brillouin Zone, following an approach developed earlier by Nozieres and Pines [64]. We hoped that our quest will cover one more piece of the puzzle of the high temperature superconductors. The results are presented in the last chapter of the thesis (chapter 5).