Experiments on ladders reveal a complex interplay between a spin-gapped normal state and superconductivity

Elbio Dagotto

National High Magnetic Field Laboratory and Department of Physics, Florida State University, Tallahassee, FL 32306, USA

Abstract

In recent years, the study of ladder materials has developed into a well-established area of research within the general context of strongly correlated electrons. This effort has been triggered by an unusual cross-fertilization between theory and experiments. In this paper, the main experimental results obtained in the context of ladders are reviewed from the perspective of a theorist. Emphasis is given to the many similarities between the two-dimensional high-T_c cuprates and the two-leg ladder compounds, including $Sr_{14-x}Ca_xCu_{24}O_{41}$ ([14–24–41]) which has a superconducting phase at high pressure and a small hole density. Examples of these similarities include regimes of linear resistivity versus temperature in metallic ladders and a normal state with spin gap or pseudogap characteristics. It is remarked that the ladder [14–24–41] is the first superconducting Cu oxide material with a non-square-lattice layered arrangement, and certainly much can be learned from a careful analysis of this compound. A short summary of the main theoretical developments in this field is also included, as well as a brief description of the properties of non-Cu-oxide ladders. Suggestions by the author on possible experiments are described in the text. Overall, it is concluded that the enormous experimental effort carried out on ladders has already unveiled quite challenging and interesting physics that adds to the rich behaviour of electrons in transition metal-oxides, and in addition contributes to the understanding of the two-dimensional cuprates. However, considerable work still needs to be carried out to fully understand the interplay between charge and spin degrees of freedom in these materials.

Contents

1. Introduction

The theoretical and experimental study of materials with an ionic structure containing dominant patterns in the shape of 'ladders' has recently attracted considerable attention in the context of strongly correlated electrons and condensed matter physics. The n-leg ladders are defined as n parallel chains of ions, with bonds among them such that the interchain coupling is comparable in strength to the couplings along the chains. The particular case of $n = 2$ motivates the use of the name 'ladder' for this geometry. The coupling between the two chains that participate in this structure is through 'rungs', language also extended to the n-leg systems. A vast literature on this subject has already accumulated, especially in the last three years. This made the study of ladders one of the two 'hottest' topics of research in condensed matter for 1996 (Greven *et al* 1997, Levy 1996) and investigations in this area continue at a rapid pace.

What is the cause of this sudden interest in ladder systems? There are basically two broad reasons that have triggered the present enthusiasm for the subject. Firstly, ladders provide a 'playground' for studies of high critical-temperature (T_c) superconductors (Bednorz and Müller 1986) since in the absence of hole carriers they have a *spin gap* in the energy spectrum, namely it costs a finite amount of energy to create spin excitations above the ground state, the latter being a spin singlet. This property resembles the spin gap feature that has been observed in the high-T_c cuprates, particularly in the underdoped regime of low hole density. Actually, for the two-dimensional cuprates a 'pseudogap' is a better term for this feature since low-energy spin excitations exist, although with low spectral weight in neutron scattering experiments. Since at hole concentrations below the optimal value the normal state above T_c presents such a pseudogap, it is expected that its existence should be important for the superconductivity that occurs once the temperature is reduced below T_c. However, no clear consensus has been reached on the origin of the pseudogap in the two-dimensional cuprates. In this framework, the ladder systems provide an interesting simpler setup for the analysis of spin and charge excitations in a spin-gapped environment since these systems certainly have a gap, both in theoretical calculations as well as in real experiments, as discussed below.

Adding to this interesting spin gap property, the early theoretical studies of ladders showed that upon doping of holes the ground state becomes dominated by *superconducting* correlations, as explained in the next section. Thus, the analogy with the underdoped high-T_c cuprates is even stronger, since the ladders not only share with them the presence of a spin gap but, also, superconductivity is expected at a low concentration of holes. Moreover, theory predicts that this superconductivity for ladders should be in the d-wave channel, currently the most accepted channel for superconductivity in the high-T_c cuprates, adding further evidence for strong similarities between doped ladders and doped planes. Last but not least, ladder systems are considerably easier to study theoretically than two-dimensional models because they are basically quasi-one-dimensional. A plethora of powerful many-body techniques, notably those involving computational methods, work well in one dimension but lose their accuracy in two dimensions (Dagotto 1994). Currently, it is believed that the physics of isolated two-leg ladders is under reasonable theoretical control, and there is little controversy about its main properties.

The second motivation for the sudden interest in ladder systems is related to the explicit realization of ladder compounds reported in seminal experimental papers reviewed here. The motivation provided by the theorists triggered an enormous effort on the experimental front to synthesize ladder materials, searching for the two main predictions made before those experiments, namely the existence of a spin gap and superconductivity. As shown below and after a considerable effort, clear evidence has now accumulated that real ladder materials with an even number of legs, two in particular, have a finite spin gap in their spectrum of spin excitations, in agreement with the theory. In addition, superconductivity in one of the

ladder compounds has been detected upon the introduction of hole carriers and using high pressure. It is certainly tempting to associate this superconducting phase, once again, with the early predictions made by theorists in this context. However, it is fair to say that the origin of superconductivity in ladders is still actively under investigation and a consensus on this subject has not yet been reached. Of particular current interest is the possible relevance of the interladder coupling to stabilize the superconducting phase. Thus, it remains to be investigated whether or not this phase corresponds to the theoretically predicted superconductivity based on the analysis of isolated ladders. In addition, several recent experiments have revealed additional close analogies between superconducting ladder compounds and high-T_c superconductors. Adding to the spin gap and superconducting properties, it has been observed that there are regions of parameter space where the resistivity of ladders is *linear* with temperature, a hallmark of the exotic normal state found in the two-dimensional cuprates.

The large number of experiments already carried out in the context of ladder materials and their many common features has influenced the presentation of this review. The paper is focused on the *experiments*, aside from a brief summary of the main theoretical results in the next section, and it certainly does *not* attempt to review the huge literature accumulated in recent years on theoretical studies of ladder compounds. Such a formidable task is postponed for a future, more comprehensive, review article. The organization of this paper is in sections that individually summarize the main results corresponding to particular ladder materials. Particular emphasis is given to Cu-oxide-based ladders, since some of them accept hole doping and the physics of carriers in spin-gapped backgrounds can be studied. However, other compounds are also described. Comments by the author on some experiments are included in the text, and a comprehensive summary is provided in section 4. The overall conclusion is that the study of ladders has already provided several interesting results to the experts in strongly correlated electrons, and further work in this context should certainly be encouraged, especially regarding the clarification of the properties of its superconducting phase.

2. Theoretical aspects: a brief summary

2.1. Undoped spin ladder models

After a plethora of theoretical studies of the $S = \frac{1}{2}$ Heisenberg model with interactions between nearest-neighbour spins, it has been clearly established that in two-dimensions and zero temperature the ground state is 'antiferromagnetic' on a square lattice. This means that the 'staggered' spin–spin correlations between spins at distance r decay to a nonzero constant as r grows. Here a modulating sign $+1$ or -1 for even and odd sites, respectively, is used in the definition of the staggered spin correlation. The decay to a finite constant at large distances indicates that the ground state has long-range order in the spin channel. In one dimension, quantum fluctuations are sufficiently strong to prevent such a long-range order, but the staggered spin–spin correlations decay slowly to zero as a power law and they remain dominant. Both in one and two dimensions there is no spin gap, namely there is no cost in energy to create a spin excitation with $S = 1$.

The current interest in the study of ladder systems started when Dagotto *et al* (1992) found that the $S = \frac{1}{2}$ Heisenberg model defined on a two-leg ladder instead of a chain or a plane has a *finite* spin gap in its spectrum of spin excitations (see also Dagotto and Moreo 1988). The reason leading to this result is simple in the 'strong-coupling' or 'strong-rung' limit, namely the limit where the Heisenberg coupling along the rungs ($J_\perp$) is much larger than along the legs (J). In this case, the ground state of the two-leg Heisenberg model corresponds to the direct product of spin singlets, one per rung, as schematically represented in figure 1(*a*). The
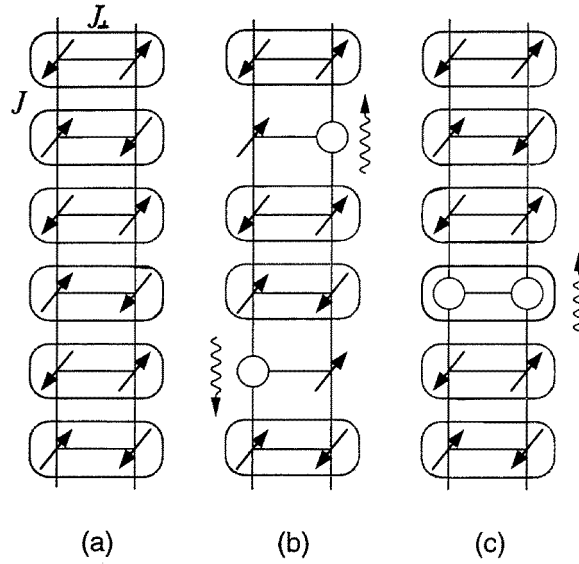
Figure 1. (*a*) Schematic representation of the ground state of a two-leg ladder. Pairs of spins along the same rung tend to form a spin singlet. (*b*) Individual holes added to the ladders destroy spin singlets. (*c*) To minimize the energy damage caused by the addition of holes, these holes tend to share the same rung forming hole bound-states. The figure is reproduced from Hiroi (1996).

overall spin of the system is zero, since each rung pair of spins is itself in a singlet. In order to produce a spin excitation, a rung singlet must be promoted to a rung triplet, and this costs an energy $J_\perp$. These local excitations can propagate along the ladder and its energy acquires a momentum dependence (Barnes *et al* 1993). The spin gap is the minimum at momentum π. Then, in the strong-coupling limit the spin are mostly uncorrelated, being in singlets most of the time, and the spin correlations decay with distance exponentially along the chains. Such a state is usually referred to as a 'spin liquid'. Gopalan *et al* (1994) and Noack *et al* (1994) suggested that a good variational description of the ground state can be obtained if the short-range resonance valence bond (RVB) state (Kivelson *et al* 1987) is used. Note that this description is certainly accurate in the strong-coupling limit, but in the isotropic limit it must be supplemented by spin singlets among spins at distances larger than one lattice spacing to account for the observed correlation length of about three lattice spacings, obtained from the staggered spin–spin correlations (Noack *et al* 1994). Nevertheless, the short-range RVB state is certainly a useful state to use in qualitative considerations of the physics of ladders. Other studies of ladders based on the RVB picture have also been presented by Sierra *et al* (1998).

In the other limit $J_\perp = 0$ the legs decouple and, as remarked above, it is well known that isolated chains do not have a spin gap and arbitrarily low-energy spin excitations can be created. However, these chains are in a 'critical' state since they do not present long-range order but a power law decay of correlations. It is anticipated that small perturbations may qualitatively change the properties of its ground state. Based on these considerations, Barnes *et al* (1993) conjectured that a spin gap opens on the two-leg ladders immediately upon the introduction of a nonzero $J_\perp$. Numerical results supported this proposal and the spin gap was observed to be $\sim J/2$ in the 'isotropic' limit $J = J_\perp$, as also found numerically by Dagotto *et al* (1992). The actual spin gap versus $J_\perp/J$ is shown in figure 2, using the frequently applied alternative notation $J_\perp = J'$. Similar results were obtained by White *et al* (1994). In addition,
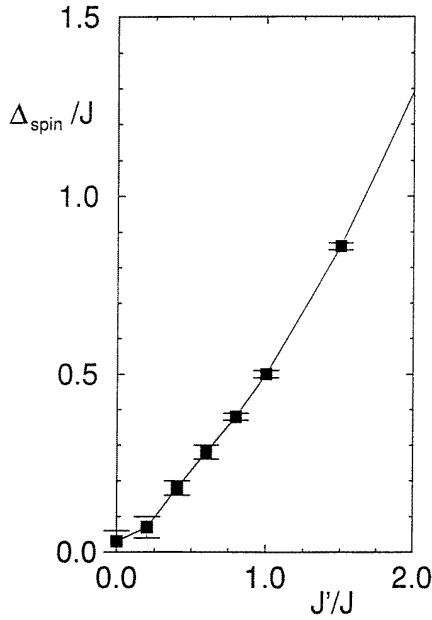
Figure 2. Spin gap Δ_{spin} versus the ratio J'/J for the two-leg ladder, with the convention that J' is the coupling along the rungs and J along the legs. The results are extrapolations to the bulk limit of data obtained on finite $2 \times N$ clusters. The figure is reproduced from Barnes *et al* (1993).

a spin gap appears in the one-band Hubbard model at half-filling if defined on a two-leg ladder (Noack *et al* 1994, Azzouz *et al* 1994). This result is reasonable since the Heisenberg model is recovered from the strong-coupling U/t limit of the one-band Hubbard model. Since the spin gap is nonzero at all couplings with the only exception of $J_\perp = 0$, the 'physics' of the two-leg ladders is said to be dominated by the strong-coupling limit with nearly decoupled rungs. Calculations in that regime are frequently carried out with the expectation that the results will not change qualitatively in the isotropic limit, which is more difficult to study directly due to the absence of a small perturbative parameter.

If the number of legs increases in the n-leg ladder structure, the physics of the two-leg ladders with its spin gap should remain qualitatively the same as long as n is *even*. In this case, the strong-coupling limit $J_\perp \gg J$ leads once again to the formation of spin singlets along the rungs since the ground state of n (even) coupled $S = \frac{1}{2}$ spins has zero total spin. As a consequence, the excitation of $S = 1$ states costs a finite amount of energy. The gap must decrease with n such that the limit of a two-dimensional gapless plane is recovered as n grows, but its magnitude will remain nonzero for any finite n (even). Numerical calculations for the four-leg ladder by Dagotto and Moreo (1988), Poilblanc *et al* (1994) and White *et al* (1994) support this picture. However, the situation is different if n is *odd*. If the strong coupling limit is studied, in each rung an odd number of spins must be considered and it is known that its ground state corresponds to a state with total spin $S = \frac{1}{2}$. Thus, at large $J_\perp$ the system can be mapped into a $S = \frac{1}{2}$ one-dimensional Heisenberg model with a coupling among spins induced by a finite leg-coupling J. This system is gapless. As a consequence, these theoretical considerations, which were originally proposed by Rice *et al* (1993) and Gopalan *et al* (1994), predict that odd-leg ladders should be gapless, while even-leg ladders have a finite spin gap as discussed above (see also Rojo 1996). Numerical calculations by White *et al* (1994) are in agreement with this prediction. Using a Monte Carlo loop algorithm and calculating the magnetic susceptibility as a function of temperature, Frischmuth *et al* (1996) also found evidence supporting the gapful versus gapless characteristics of the ground state of even- and odd-leg ladders, respectively. Their results are reproduced in figure 3.
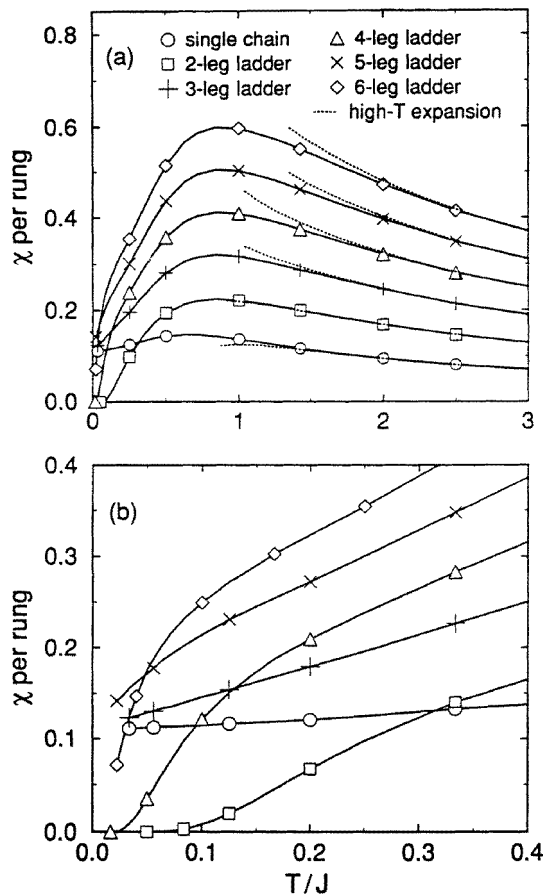
Figure 3. Susceptibility as a function of temperature for the single chain and the Heisenberg ladders with up to six legs, obtained by Frischmuth *et al* (1996) using a Monte Carlo algorithm. The two parts of the figure differ in the temperature range analysed. At low temperature, (*b*) clearly shows that the odd- and even-leg ladders have a qualitatively different behaviour, as described in the text.

2.2. Hole-doped spin ladder models

The theoretical study of ladder models in the presence of hole doping leads to interesting predictions. Dagotto *et al* (1992) studied the t–J model on a two-leg ladder using computational techniques. In this model the degrees of freedom at each site are either a $S = \frac{1}{2}$ spin that mimics the Cu^{2+} ion with nine electrons in its d-shell or a 'hole' that represents a Cu^{3+} state, usually assumed to be made out of a spin singlet combination of an oxygen hole and the $S = \frac{1}{2}$ Cu ion forming a so-called Zhang–Rice singlet. Analysing the t–J model correlations corresponding to the operator that create or destroy hole pairs at nearest-neighbour sites and working at a small concentration of doped holes, Dagotto *et al* (1992) observed that these correlations were very robust, clearly indicative of a ground state dominated by strong superconducting tendencies. The rationalization of this surprising result is sketched in figures 1(*b*) and (*c*). The main idea is that the state upon which the holes are added is dominated by the formation of rung singlets, at least in strong coupling. If a hole is added, equivalent to removing a $S = \frac{1}{2}$, the other spin of the original singlet becomes free and it no longer reduces its energy by singlet formation. If two holes a large distance apart are added to the system, each one will produce substantial energy damage to the spin background, as shown in figure 1(*b*), since both break a singlet. However, if the two holes are nearby they can share a common rung, reducing the number of damaged spin singlets from two to one. This idea leads in a natural

way to the concept of hole binding on two-leg ladders (figure 1(*c*)). Once the formation of hole pairs is accepted as a logical consequence of the spin-singlet-dominated characteristics of the undoped ground state, the presence of superconductivity becomes natural, as explained by Dagotto *et al* (1992) (see also Dagotto and Rice 1996).

Sigrist *et al* (1994) using a mean-field approximation predicted that the above-described superconductivity in two-leg ladders should exist in the 'd-wave' channel, namely that the pair correlations should change sign if the creation (or destruction) hole pair operator is aligned along the legs or along the rungs. Although the two-leg ladder is certainly not invariant under rotation as the planes are, the language of referring to the superconductivity in ladders as 'd-wave' is based on the use of the same concept (sign change under rotation of 90°) for square lattices. Actually, since the antiferromagnetic correlation length on ladders is about three lattice spacings, which is sufficiently large for the individual holes to be mainly surrounded by spins in an antiparallel arrangement, some of the arguments that lead to d-wave pairing in the two-dimensional cuprates (see, for instance, Nazarenko *et al* (1996)) are also operative on ladders. This d-wave character of pairing on ladders has been confirmed by a variety of calculations performed by Riera (1994), Tsunetsugu *et al* (1995), Hayward *et al* (1995) and others. Some results are shown in figure 4. Calculations in the one-band Hubbard model arrived at similar conclusions (see Asai 1994, Yamaji and Shimoi 1994). Additional information about hole binding can be found in Gayen and Bose (1995) where an exact solution of the two-hole eigenvalue problem is provided. More details can be found in Bose and Gayen (1999). Superconducting correlations have also been studied in three-leg ladders (Kimura *et al* 1996a, b). Very recently, Gazza *et al* (1999) analysed the hole binding and pairing correlations on two-leg ladders taking into account the Coulomb repulsion between carriers at distances of one lattice spacing, which is expected to be non-negligible. This interaction is rarely considered in the study of the t–J model. Gazza *et al* (1999) found that in spite of this repulsion the binding and pair correlations are still robust on ladders, as is the case when only on-site Coulomb interactions are included. This provides additional support to the idea that real doped ladders should be superconducting.

It is likely that these superconducting tendencies will be robust as long as the spin background does not drastically alter its spin gap properties. However, it is also expected that the spin gap will reduce its size as the hole doping increases (Dagotto *et al* 1992, Noack *et al* 1994, Poilblanc *et al* 1994, Hayward and Poilblanc 1996). In this context, the spin excitations created upon hole doping were analysed by Tsunetsugu *et al* (1994). Besides the excitation that already appears in the undoped limit, namely the promotion of a rung spin singlet to a triplet, other possible excitations may arise. For instance, the hole pairs described in the previous paragraph may change their spin singlet characteristics to a triplet. In other words, a bound state of a two-hole bound state and a rung spin triplet may develop. The existence of this excitation has been recently confirmed by Dagotto *et al* (1998) using a new technique that uses just a fraction of the total Hilbert space of a given cluster (Riera and Dagotto (1993) and references therein) after the Hamiltonian has been rewritten in the basis that diagonalizes the individual rungs. The undoped limit has also been studied in the plaquette basis, instead of the rung basis, as reported by Piekarewicz and Shepard (1997). A typical result in the rung basis is shown in figure 5, working on a 2×16 cluster. Of the two branches, one (I) is a remnant of the result observed without holes and the other one (II) is generated by hole doping and corresponds to the hole pair rung triplet bound state. Other studies using the rung basis have involved the calculation of the one-particle spectral function, and the results will be briefly summarized later when photoemission experiments are discussed.

The list of interesting theoretical studies of ladder systems is certainly much longer than shown thus far in this section. Other aspects of ladder systems that have been analysed
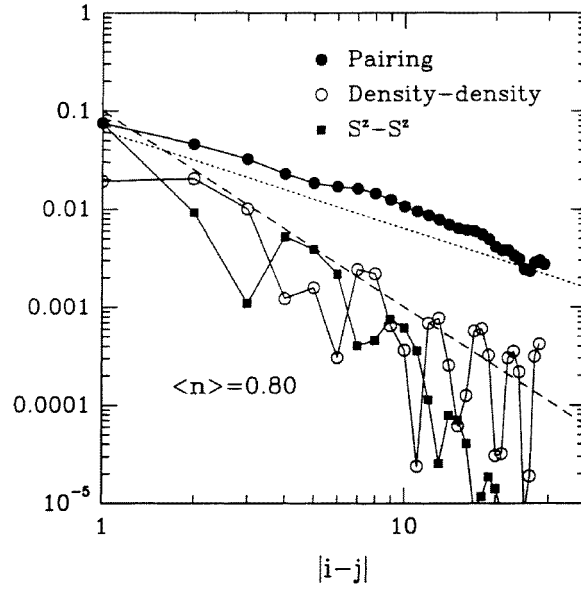
Figure 4. Log–log plot of various correlation functions versus the real space separation $|i - j|$ for a 2×30 open chain with density $\langle n \rangle = 0.8$ and $J/t = 1.0$. The dashed line has a slope -2 and the dotted line -1. The figure is taken from Hayward *et al* (1995), where more details can be found on the definition of the correlation functions used here.
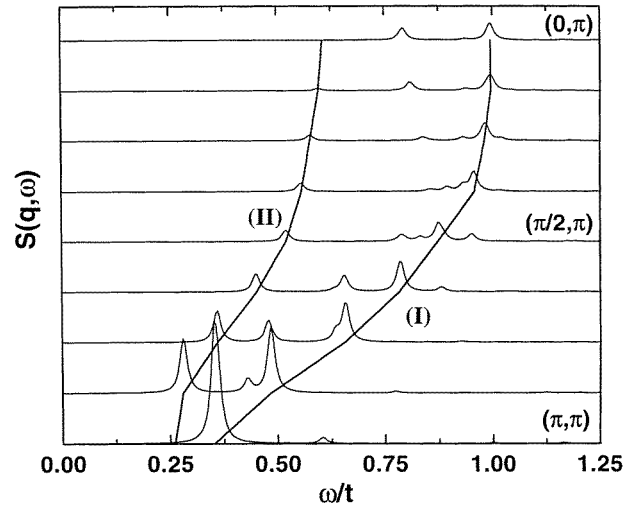
Figure 5. The dynamical spin structure factor $S(q, \omega)$ for the $q_y = \pi$ branch of a 2×16 cluster with two holes. The physical meaning of branches (I) and (II) is explained in the text. The figure is taken from Dagotto *et al* (1998) who used a technique involving a small fraction of the Hilbert space, after the t–J model is rewritten (exactly) in the rung basis.

in the literature include the careful study of antiferromagnetic correlation lengths versus temperature in the undoped limit (Greven *et al* 1996, Syljuasen *et al* 1997), weak coupling renormalization-group treatments (Kuroki and Aoki 1994, Balents and Fisher 1996a, Lin *et al* 1997, Lin *et al* 1998, Emery *et al* 1998), coupling of the chains with emphasis on

the Luttinger liquid properties (Schulz 1996), the influence of four-spin interactions in the undoped ground state (Nersesyan and Tsvelik 1997), staggered spin ladders (Martin-Delgado *et al* 1996), the influence of disorder on ladders (Orignac and Giamarchi 1998), two-leg Hubbard ladders and their relation with carbon nanotubes (Balents and Fisher 1996b, Konik *et al* 1998) comparison with weak-coupling calculations (Park *et al* 1998), the influence of interladder coupling on the possible dimensional crossover of $Sr_{14-x}Ca_xCu_{24}O_{41}$ (Kishine and Yonemitsu 1998), the relation between the resistivity of this material and the two-dimensional $YBa_2Cu_4O_8$ cuprate (Moshchalkov *et al* 1998) as well as several others. In addition, ladder physics is also considered in the context of stripe phases for the two-dimensional cuprates since the region in between the presumed to exist one-dimensional-like metallic stripes are *n*-leg ladders. The spin gap proximity effect discussed by Emery *et al* (1997) proposes that a spin gap is created in the one-dimensional metallic striped environment due to the influence of a nearby system with spin-gapped properties, such as an even-leg ladder. The list of interesting ladder-related theoretical results goes on and on. However, since the focus of this review is on the experimental results rather on theoretical developments, the author will postpone a comprehensive review of the latter for the near future and concentrate on the experimental aspects of ladder physics in the rest of the paper.

3. Experimental results

After an enormous experimental effort, reviewed here, several materials with ladders in their structures have become available in recent years, and a variety of exciting experiments have already been carried out in this context. In this section the main experimental results will be discussed, organizing the presentation according to the family of ladder compound studied, and the technique used in its analysis. The main emphasis will be given to the Cu-oxide-based ladders since they admit hole doping by chemical substitution. Among them $Sr_{14-x}Ca_xCu_{24}O_{41}$, the so-called '[14–24–41]' compound, will be discussed in particular detail since superconductivity has been found in this material, as described below. Note, however, that the compound that was mentioned in the early work of Dagotto *et al* (1992) as a possible realization of a ladder model was of a different variety, namely $(VO)_2P_2O_7$ (sometimes known as VOPO). This material, originally discussed by Johnston *et al* (1987), has a two-leg V-oxide ladder in its structure. Neutron scattering experiments on VOPO presented by Eccleston *et al* (1994) reported a spin gap in the spectra which was interpreted in terms of a two-leg ladder dominant structure. However, more recent inelastic neutron scattering experiments by Garrett *et al* (1997a) have shown that the properties of this compound are better described by an alternating Heisenberg antiferromagnetic chain, running perpendicular to the ladders (see also Garrett *et al* 1997b). Based on this reanalysis, it is reasonable to assume that VOPO is no longer part of the family of ladder compounds, and thus the description below will concentrate on other materials, notably those with chemical compositions containing copper and oxygen, similar to the high-T_c cuprates, since they are susceptible to chemical substitutions and the concomitant addition of hole carriers.

3.1. The Cu oxide ladder compound $SrCu_2O_3$

A seminal contribution to the development of the field of ladders was provided by Azuma *et al* (1994) (see also Hiroi *et al* 1991) when these authors reported the preparation of a Cu oxide $S = \frac{1}{2}$ two-leg ladder. This result was not only important for providing a concrete realization of the ladder compounds discussed by the theorists, but also due to the possibility of changing the hole concentration through chemical substitution in such a Cu oxide, as occurs
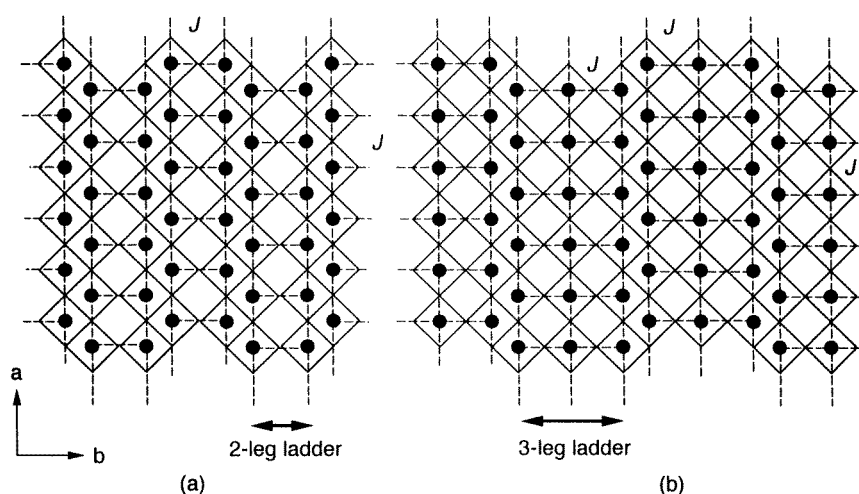
Figure 6. Schematic representation of (*a*) the Cu_2O_3 sheets of $SrCu_2O_3$ (from Azuma *et al* 1994). The three-leg ladder $Sr_2Cu_3O_5$ is also shown in (*b*). The filled circles are Cu^{2+} ions, and O^{2-} ions are located at the corners of the squares drawn with solid lines.
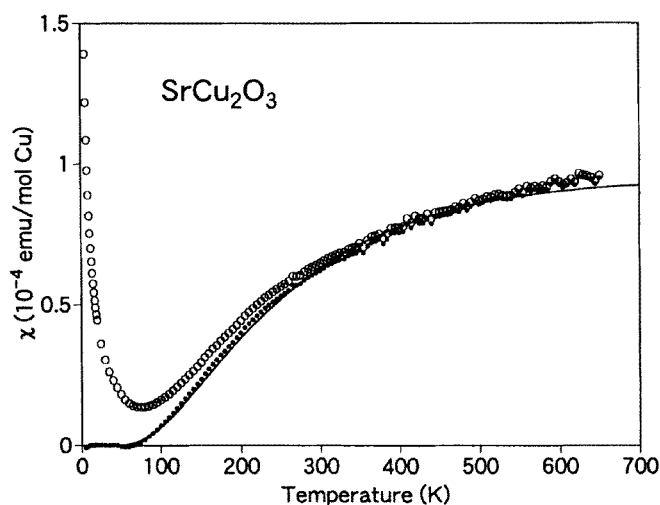
Figure 7. The temperature dependence of the magnetic susceptibility of $SrCu_2O_3$ (from Azuma *et al* 1994). Details can be found in the text.

in the high-T_c cuprates. The chemical composition of the compound reported by Azuma *et al* (1994) was $SrCu_2O_3$, and a schematic representation is provided in figure 6. Note that within the ladders the 180° Cu–O–Cu bond should provide a strong Heisenberg coupling among the Cu ions, while in between the ladders the bond is of 90° and, thus, expected to be weak and ferromagnetic.

In figure 7 the experimentally determined temperature dependence of the magnetic susceptibility of $SrCu_2O_3$ is shown (from Azuma *et al* 1994). The open circles are the experimental raw numbers, while the closed circles show the data after subtraction of the Curie component due to impurities. The solid curve is a theoretical fit that gives a spin gap of
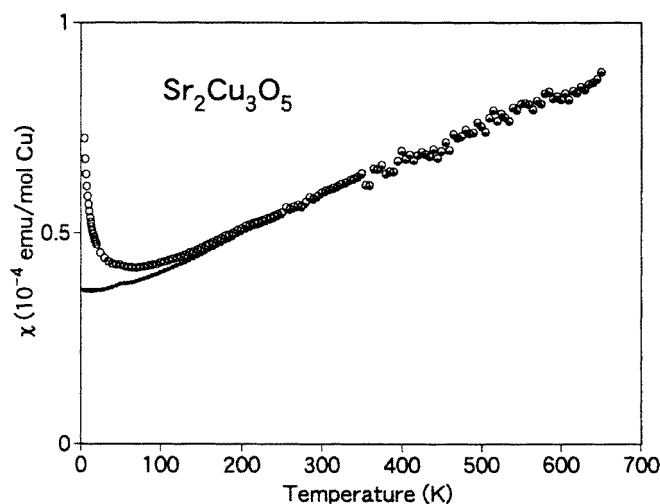
Figure 8. As figure 7 but for the three-leg compound $Sr_2Cu_3O_5$ (from Azuma *et al* 1994). In this case a large susceptibility is observed even at low temperatures, indicative of the absence of a spin gap, in agreement with theoretical expectations.

420 K. This is in rough agreement with the theoretical expectation of $\Delta \sim J/2$ reported by Barnes *et al* (1993), if it is assumed that the Heisenberg coupling is similar in magnitude to its two-dimensional Cu oxide counterpart $J \sim 1200$ K. This is in principle a natural assumption due to the similarities between the Cu–O–Cu bonds on ladders and planes. Note that Azuma *et al* (1994) also observed (figure 8) that the magnetic susceptibility of a three-leg ladder material ($Sr_2Cu_3O_5$) does not show indications of a spin gap, as expected from a ladder with an odd number of legs (Rice *et al* 1993, Gopalan *et al* 1994, Sigrist *et al* 1994, Dagotto and Rice 1996). Muon spin relaxation measurements of the two- and three-leg compounds by Kojima *et al* (1995) have also confirmed the gapful versus gapless character of the spin state of even- and odd-leg ladder systems. Recent experiments by Thurber *et al* (1999) suggest that the three-leg ladder compound has a dimensional crossover from quasi-one-dimensional to anisotropic two-dimensional at 300 K.

[63]Cu nuclear magnetic resonance (NMR) studies by Ishida *et al* (1994, 1996) also contributed to the analysis of the two- and three-leg ladder compounds described here. The spin gap of $SrCu_2O_3$ was in this case found to be 680 K, i.e. larger than the result deduced from the magnetic susceptibility by Azuma *et al* (1994), although of the same order of magnitude. The instantaneous spin–spin correlation was estimated to be 3–4 lattice spacings, in good agreement with theoretical expectations (White *et al* (1994), Dagotto and Rice (1996) and references therein).

Regarding the difference between the spin gap reported by magnetic susceptibility and NMR techniques, as well as the extra difficulty in understanding the origin of the actual value of the exchange Heisenberg constant which seems smaller than in other 180° Cu–O–Cu bond materials, Johnston (1996) made the important observation that the susceptibility data of $SrCu_2O_3$ can be fit accurately with a two-leg ladder prediction using a rung coupling, denoted by J' in figure 9, smaller by a factor two than the coupling along the legs J (see Barnes and Riera 1994). Using the ratio $J'/J \sim 0.5$, the exchange constant needed to fit the data is now $J \sim 2000$ K, in agreement with results obtained for other cuprates by Motoyama *et al* (1996) (for details see Johnston (1996)). Mizuno *et al* (1998) reached similar conclusions
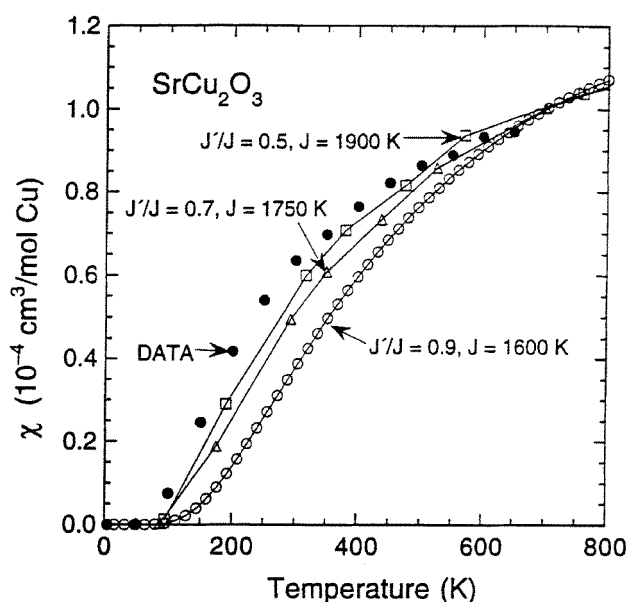
Figure 9. Magnetic susceptibility versus temperature for $SrCu_2O_3$ (filled circles). Shown as open symbols are fits to these data using the calculations of Barnes and Riera (1994) for the isolated spin-$\frac{1}{2}$ two-leg ladder at several ratios of the rung Heisenberg coupling, here denoted by J', and the leg coupling J. The figure is reproduced from Johnston (1996). A comprehensive experimental paper with updated information about these issues is in preparation (D Johnston, private communication).

regarding J'/J by investigating the influence of the Madelung potential of ladders on the problem. Then, although the microscopic origin of the anisotropy between legs and rungs is still under discussion, evidence is accumulating that this compound corresponds to a ladder in the coupling regime $J'/J < 1$ (note, however, that a ratio J'/J very close to one has been obtained by Matsuda *et al* (1999) by including four-spin exchange interactions in the ladder model Hamiltonian to fit neutron scattering data for $La_6Ca_8Cu_{24}O_{41}$). It is unclear to this author if, for values of J'/J smaller than one, superconductivity would be expected upon hole doping for realistic values of J/t in the t–J model discussed in the previous section. Calculations should be carried out in the interesting regime $J'/J \sim 0.5$ to address this issue. Adding to the analysis of this material, Ishida *et al* (1996) reported the effect of doping carriers on the two-leg compound by substitution of Sr by La. Their results suggest that the added electrons unfortunately remain localized, and thus electron-doped $SrCu_2O_3$ may not provide a good realization of the physics arising from the (hole) doping of the t–J model. Other compounds are likely needed to realize the theoretical scenario discussed in section 2.2.

3.1.1. Doping of $SrCu_2O_3$ with zinc. The doping of $SrCu_2O_3$ through the replacement of Cu^{2+} by Zn^{2+} has produced interesting results. Particularly important has been the observation by Azuma *et al* (1997) of a rapid suppression of the spin gap in this two-leg ladder compound as the concentration of Zn (here denoted by x) was increased. The results for the magnetic susceptibility are shown in figure 10. As x increases, the susceptibility also increases at low temperature revealing the presence of low-energy spin states. At those temperatures an unexpected transition to an antiferromagnetic state is also observed, with a maximum Néel temperature of 8 K. Thus, it is apparent that a very small amount of impurities affects severely
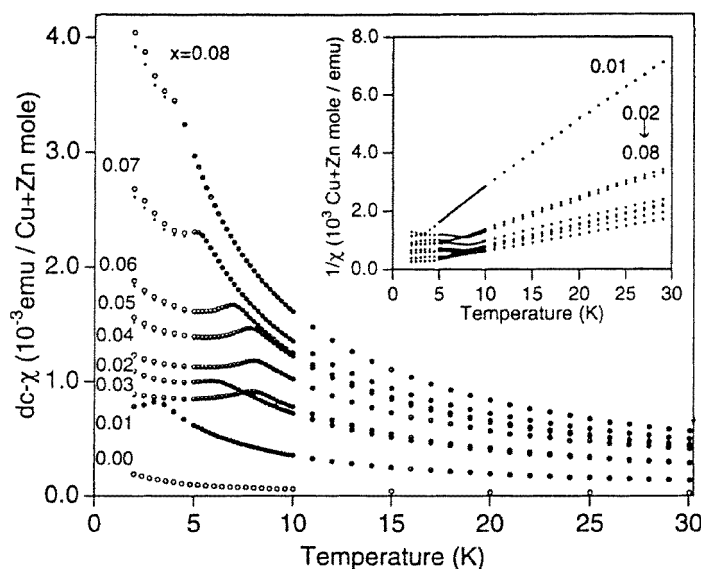
Figure 10. Magnetic susceptibility of $Sr(Cu_{1-x}Zn_x)_2O_3$ versus temperature at several Zn concentrations. The inset shows the temperature dependence of the inverse susceptibility. The results are reproduced from Azuma *et al* (1997).

the low-temperature properties of $SrCu_2O_3$ (see also Fujiwara *et al* 1998). Recently, Ohsugi *et al* (1998) reported a comprehensive study of $SrCu_2O_3$ doped with Zn, Ni and La. The results were analysed in terms of an impurity-induced staggered polarization around the vacancies. The size of this perturbation centred at, e.g., the Zn ion was found to be very large, much longer than the 3–5 lattice spacings characteristic of the antiferromagnetic correlation length without the impurities. Actually, the new correlation length is as large as 50 lattice spacings at Zn doping $x = 0.001$. Although rather surprising, note that these results are qualitatively similar to those reported by Laukamp *et al* (1998) using computational techniques in their study of the influence of vacancies on the spin arrangement in its vicinity, using two-leg ladders and neglecting interladder couplings. For Ni doping, similar theoretical results were obtained by Hansen *et al* (1998). It is interesting to observe that a similar behaviour has been found in spin-Peierls chains, which also have a spin gap although of an origin quite different from the one found in ladders (for references on experiments and theoretical developments in this context see Laukamp *et al* (1998)). A possible rationalization of this curious phenomenon is the following: in the global spin singlet state of the undoped ladder, it is known that the formation of local spin singlets along the rungs is favoured in the sense that such a configuration has a substantial weight in that ground state. If one of the spins is replaced by a zero-spin vacancy, such as Zn^{2+}, the other spin belonging to the same rung becomes 'free' and, thus, it contributes to the magnetic susceptibility at low temperatures as a $S = \frac{1}{2}$ impurity would do. These impurities are certainly weakly interacting among themselves since their mean distance is large, but at very low temperature such a residual interaction may nevertheless favour a Néel-order state, as discussed by Martins *et al* (1996, 1997) and Laukamp *et al* (1998). The reader should also consult the related literature contained in the work of Motome *et al* (1996), Ng (1996), Nagaosa *et al* (1996), Miyazaki *et al* (1997), and references therein. Some of these authors also discussed the related *enhancement* of spin correlations in the vicinity of the vacancies, as observed in computational studies of spin systems for both ladders and dimerized chains. This
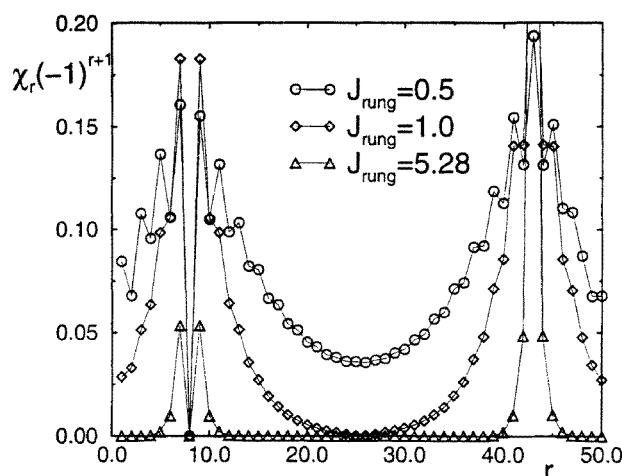
Figure 11. The local staggered susceptibility $\chi_r(-1)^r$ along the upper leg of a 2×50 ladder obtained with computational techniques (from Laukamp *et al* 1998). Two vacancies are included in the system, located at rung 8 on the upper leg and 43 on the lower leg. Results for three values of the ratio $J_{\text{rung}} = J_{\perp}/J$ are shown. For details see Laukamp *et al* (1998).

enhancement favours the tendency towards antiferromagnetic order as the concentration of vacancies grows. As a consequence, from an apparently disordering effect such as the random replacement of Cu ions by Zn ions, an order state is stabilized at low temperatures.

Laukamp *et al* (1998) have also analysed the ratio $J_{\perp}/J$ that fits the data the best, and, in agreement with Johnston (1996), it was observed that a ratio 0.5 leads to an antiferromagnetic disturbance near the vacancies that covers the entire lattice even at very low Zn concentrations. As an example, the (staggered) local susceptibility calculated using numerical techniques is shown in figure 11 for three values of $J_{\perp}/J$, namely 0.5, 1.0 and 5.28, the latter corresponding to the organic compound $Cu_2(C_5H_{12}N_2)_2Cl_4$, which will be discussed in section 3.4. Clearly, at 0.5 all spins become involved in the staggered spin order at this vacancy density, a result compatible with experiments. The results in figure 11 are actually very similar to the data in figure 13 of Ohsugi *et al* (1998) that reported the spatial variation of the antiferromagnetic moments in 1% and 2% Zn-doped $SrCu_2O_3$. Thus, theoretical studies are able to reproduce the qualitative features of the experiments in ladders with vacancies.

3.2. The metallic ladder compound $La_{1-x}Sr_xCuO_{2.5}$

Under a high pressure of 6 GPa, Hiroi and Takano (1995) made the important discovery that the compound $La_2Cu_2O_5$ undergoes a transformation into a simple perovskite structure. The ionic arrangement of this compound is shown in figure 12. Two-leg Cu oxide ladders appear in the structure, involving $180°$ angle Cu–O–Cu bonds. The length and angle of the corresponding Cu–Cu bonds between ladders suggest that the interladder coupling is weaker than the intraladder one. Thus, as a first approximation, it is reasonable to assume that this compound is formed by an array of weakly interacting two-leg ladders. More details about this material and the experiments can be found in the comprehensive review by Hiroi (1996). The temperature dependence of the magnetic susceptibility of $LaCuO_{2.5}$ is shown in figure 13, reproduced from Hiroi (1996). After removing the contribution of impurities, the resulting susceptibility indeed behaves as expected for a two-leg Heisenberg ladder. In particular, it
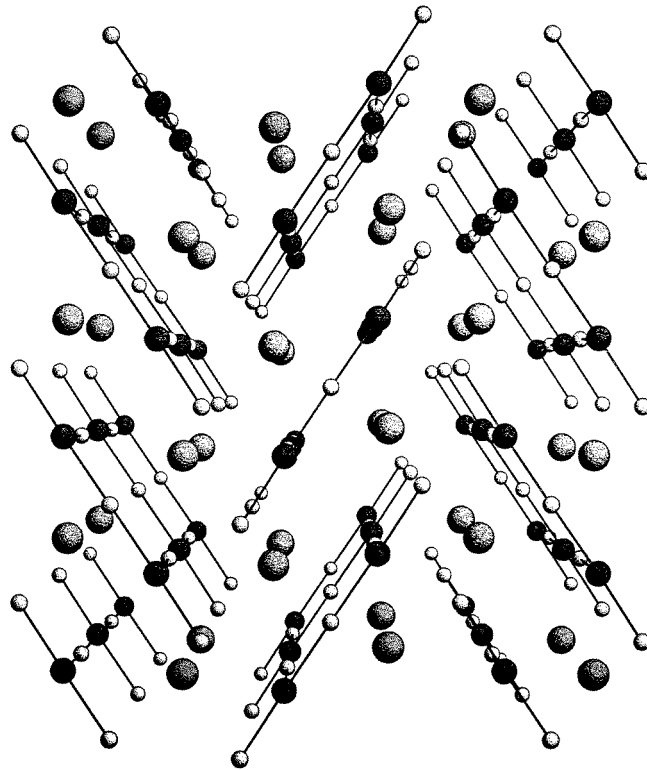
Figure 12. The structure of $LaCuO_{2.5}$ along the c-axis. Large, medium, and small balls represent La, Cu, and O atoms, respectively. The figure is reproduced from Hiroi (1996).

presents a spin gap behaviour at low temperatures with $\Delta = 492$ K, a number similar to the gap obtained for $SrCu_2O_3$ ($\sim$400 K), as already described.

An important observation is that the ladder compound $LaCuO_{2.5}$ can be hole doped replacing La by Sr (Hiroi 1996). This doping is achieved also working at high pressure. There are no significant changes in the structure after doping. The amount of Sr that can be added to $LaCuO_{2.5}$ is fairly large, up to $x = 0.20$. Following this doping procedure a dramatic insulator-to-metal transition has been observed in the resistivity, as shown in figure 14, taken from Hiroi (1996). Based on the sign of the slope of the resistivity versus temperature, the metal–insulator transition was found to be located roughly between $x = 0.18$ and 0.20. Note the sharp decrease in the resistivity with doping which corresponds to more than seven orders of magnitude. Comparing the results for this compound with those for the two-dimensional cuprate $La_{2-x}Sr_xCuO_4$, it was observed that at the hole density $x \sim 0.20$ the resistivities of both compounds are actually very similar, as the reader can observe in figure 15 (Hiroi 1996). The doping dependence of the magnetic susceptibility is contained in figure 16. The spin gap characteristics of the ground state seem to disappear with increasing doping. Photoemission and x-ray absorption studies performed on $La_{1-x}Sr_xCuO_{2.5}$ by Mizokawa *et al* (1997) found changes in the overall electronic structure induced by hole doping similar to those in $La_{2-x}Sr_xCuO_4$. Spectral weight around the Fermi level (E_F) was found to increase with x, and a weak but finite Fermi edge is established at $x = 0.20$. This result is compatible with the metallic character of the compound deduced from the resistivity at this hole concentration.
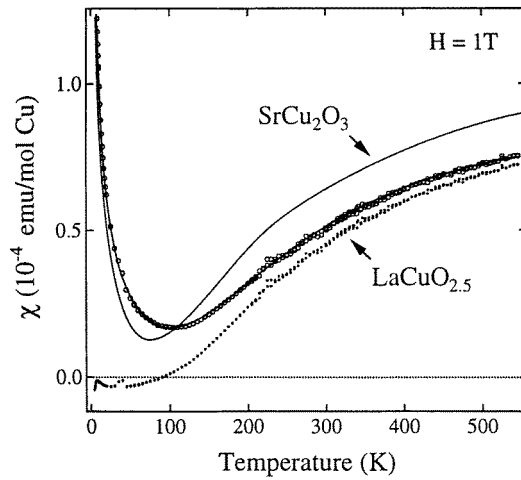
Figure 13. The temperature dependence of the magnetic susceptibility for LaCuO$_{2.5}$, from Hiroi (1996). The open circles are the raw data. The solid curve through them is a fit including a temperature-independent term, a Curie term due to impurities, plus the bulk susceptibility expected from a two-leg Heisenberg ladder. The dotted curve is the susceptibility after subtracting the Curie component. The other solid curve corresponds to SrCu$_2$O$_3$, for comparison, taken from Azuma *et al* (1994) (see figure 7).
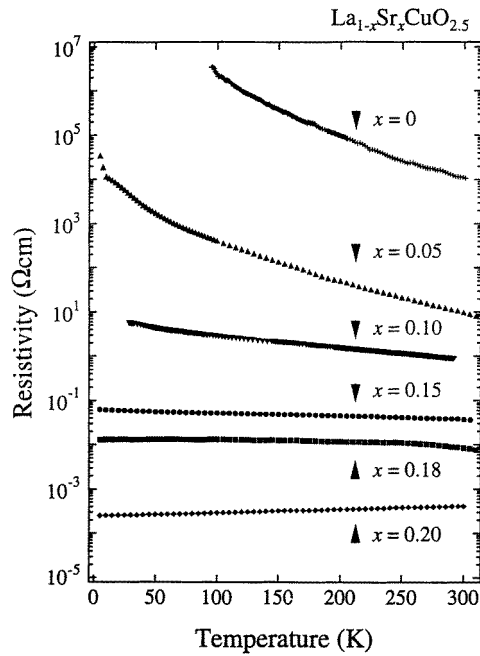

Figure 14. Resistivity of La$_{1-x}$Sr$_x$CuO$_{2.5}$ versus temperature for several Sr compositions (reproduced from Hiroi (1996)).

Thus, it is clear that La$_{1-x}$Sr$_x$CuO$_{2.5}$ is a metal at $x \sim 0.20$, improving on the characteristics of SrCu$_2$O$_3$ (cf section 3.1) which is a two-leg ladder compound that cannot be hole doped.

Although the resistivity results presented in figure 14 correspond to an encouraging metal–insulator transition upon doping, unfortunately those results also show that this ladder compound does not become a superconductor in spite of the theoretical predictions in this
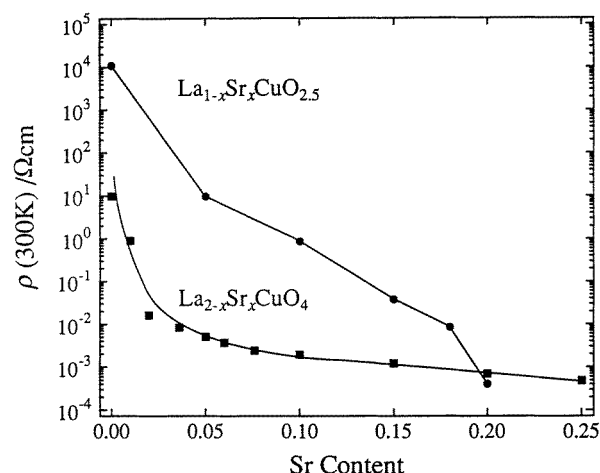
Figure 15. The resistivity of $La_{1-x}Sr_xCuO_{2.5}$ and $La_{2-x}Sr_xCuO_4$ at 300 K, and its doping dependence (reproduced from Hiroi (1996)).
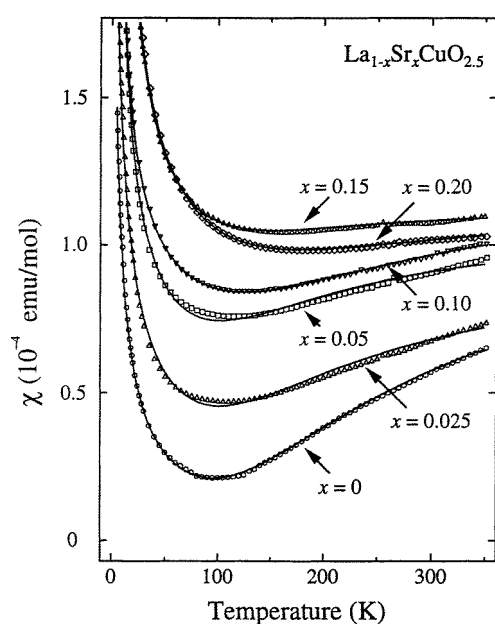
Figure 16. The doping dependence of the magnetic susceptibility at several hole concentrations (taken from Hiroi (1996)).

respect. There are two possible reasons to explain the absence of superconductivity here. Firstly, the interladder coupling, while certainly smaller than the intraladder one, may not be negligibly small since it does not involve 90° bonds. It is not clear to what extent this finite extra interladder coupling would change the theoretical predictions for isolated ladders. Second, the replacement of La by Sr produces an intrinsic randomness in the system that may localize the holes.

Regarding the first possibility, namely the relevance of the interladder couplings in this compound, Normand and Rice (1996) proposed that the magnetic state of $LaCuO_{2.5}$ may be located in parameter space near the crossover from spin liquid to the antiferromagnetic state expected on a three-dimensional spin system without frustration (see also Normand and Rice

(1997)). This proposal is motivated by the NMR results of Matsumoto *et al* (1996) and μSR results of Kadono *et al* (1996) that actually reported the presence of antiferromagnetic order in this compound at a temperature $T_N \sim 110$ K. Thus, it is apparent that the spin singlet state is in close competition with a Néel state in this compound. Troyer *et al* (1997), using a combination of analytical and quantum Monte Carlo techniques, expanded on Normand and Rice's idea and showed that the apparently conflicting experimental results, namely evidence of spin liquid formation at intermediate temperatures and a Néel state at low temperature, can be reconciled if the system is near a quantum critical point. However, more recently Normand *et al* (1998) argued that, even including realistic interladder couplings, the doped LaCuO$_{2.5}$ compound should present superconductivity, at least within the spin fluctuation approximation. Thus, these authors concluded that the random potential due to the replacement of Sr^{2+} by La^{3+} must be responsible for suppressing the superconducting phase, and suggested that more work should be devoted to the preparation of single crystals of this compound at low doping values to search for indications of superconductivity, which is expected to be the strongest in such a regime of density according to their theoretical calculations. Overall, it is clear that the experimental analysis of the properties of this ladder compound should continue in order to clarify what causes the suppression of superconductivity, and to investigate what sort of metallic state is obtained near the spin-gapped regime that resembles the behaviour of the two-dimensional cuprates.

3.3. The superconducting ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$

After the quite interesting first attempts described in sections 3.1 and 3.2 to search for superconductivity in two-leg ladders, success was finally reached using the compound (La, Sr, Ca)$_{14}$Cu$_{24}$O$_{41}$, the [14–24–41] or 'phone number' compound. The synthesis of this material was initially reported by McCarron *et al* (1988) and Siegrist *et al* (1988). This compound contains one-dimensional CuO$_2$ chains, (Sr, Ca) layers, and two-leg Cu$_2$O$_3$ ladders as shown in figure 17. A very important property of this material is that it can be synthesized at ambient pressure, unlike some of the compounds described in previous sections. In addition, a spin gap was confirmed to exist in the Sr$_{14}$Cu$_{24}$O$_{41}$ compound as shown, for example, using inelastic neutron scattering by Eccleston *et al* (1996). The nominal Cu valence for this material is +2.25, which arises from $[2 \times 41(\text{oxygens}) - 2 \times 14(\text{Sr})]/24(\text{Cu})$, instead of just +2.0. This means that holes are already doped into the structure (a 'self-doped' system), as occurs in more familiar high-T_c compounds such as YBa$_2$Cu$_3$O$_7$. Replacement of Sr by Na, which is in a 1+ state, is possible and NMR studies have been recently reported for this compound by Carretta *et al* (1998). However, in practice the substitution of Sr by Ca, both of them in a 2+ valence state, turned out to be more efficient in providing carriers to the ladders since such a doping may alter the distribution between the chains and ladders of the already existing holes. Carter *et al* (1996) in their important early investigations in this context indeed managed to replace Sr by Ca, increasing by this procedure the number of hole carriers on the ladders–chains structure. These authors reported a decrease of the resistivity by this procedure, and interpreted their results as corresponding to the addition of extra holes to the chains instead of the ladders. However, the current prevailing point of view is that Ca doping produces a rearrangement of holes, moving them into the ladders, as we shall go on to explain in detail. The discussion that follows on the notable [14–24–41] compound starts with the remarkable discovery of superconductivity, followed by a review of the results obtained in this context using a variety of experimental techniques.

(a) Crystal structure
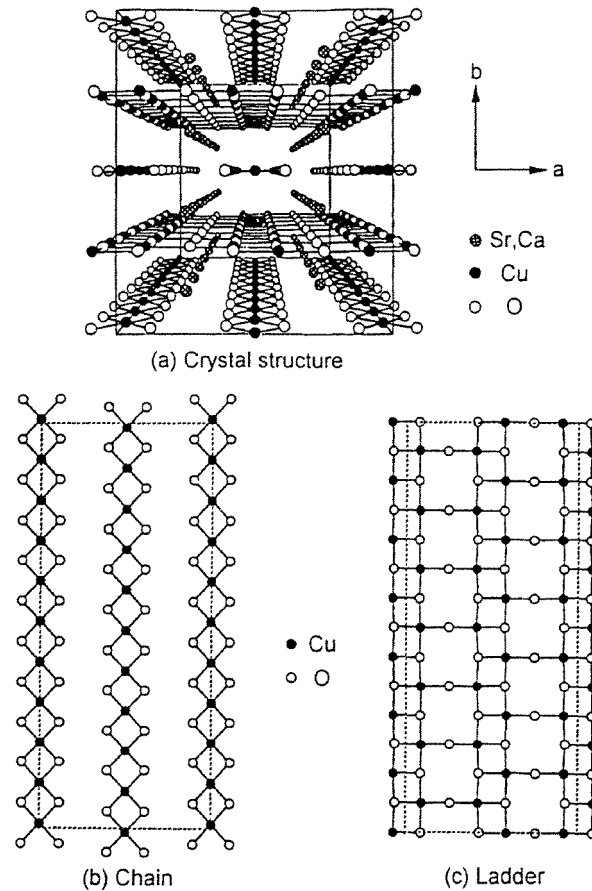
(b) Chain

(c) Ladder

Figure 17. (*a*) The crystal structure of $(Sr, Ca)_{14}Cu_{24}O_{41}$. (*b*) and (*c*) show the CuO_2 chain and Cu_2O_3 ladder subunit, respectively. The figure is reproduced from Magishi *et al* (1998).

3.3.1. Superconductivity in doped [14–24–41] with x = 13.6.   A crucial breakthrough in the field of ladders occurred when Uehara *et al* (1996) discovered superconductivity in the $x = 13.6$ Ca-doped compound $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$. To stabilize superconductivity Uehara *et al* (1996) observed that a high pressure of 3 GPa is needed. This discovery substantially contributed to the current enormous effort devoted to the understanding of ladder compounds (Levy 1996). The resistivity ρ versus temperature at several pressures is shown in figure 18. The drop in ρ at the critical temperatures T_c is clear. There is an 'optimal' pressure at which the T_c is the highest. More recent studies of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41+\delta}$ by Isobe *et al* (1998) reported the resistivity versus temperature shown in figure 19. The results are very similar to those previously reported by Uehara *et al* (1996). The hump centred at $\sim$100 K disappears at 5 GPa and the sample goes into a metallic regime. Note that the resistivity at $x = 13.6$ and high pressure changes from an approximate T^2-dependence near the optimal pressure to a linear dependence at higher pressures when superconductivity is suppressed (see Isobe *et al* 1998). This is different from the behaviour observed in the two-dimensional high-T_c compounds and also different from observation at other Ca concentrations. The critical temperature versus pressure from Isobe *et al* (1998) is reproduced in figure 20. The bell-like shape of the curve clearly resembles the well known results for the two-dimensional cuprates, if it is assumed
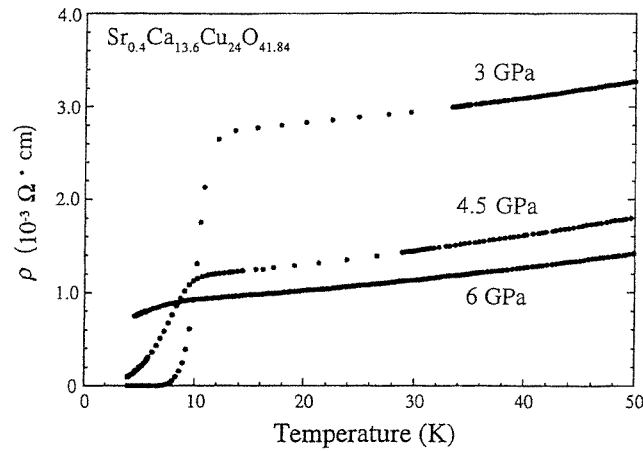
Figure 18. Electrical resistivity ρ of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ versus temperature below 50 K, and under pressure of 3, 4.5 and 6 GPa, showing the existence of superconductivity. The figure is reproduced from Uehara *et al* (1996).
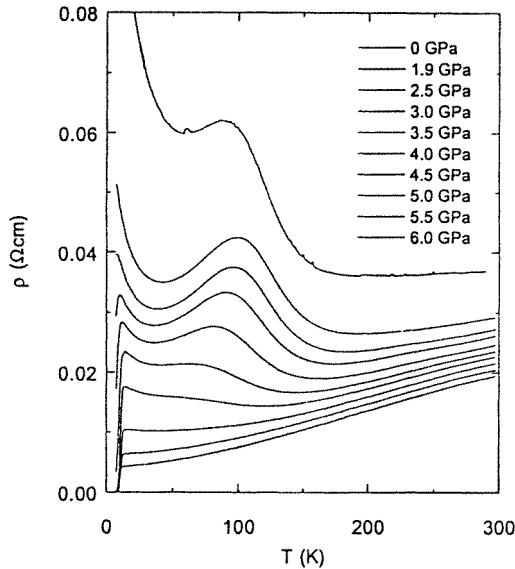
Figure 19. The temperature dependence of the electrical resistivities at various pressures, for $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41+\delta}$. The data are reproduced from Isobe *et al* (1998).

that pressure is replaced by hole concentration. The optimal pressure is around 5 GPa, with an optimal T_c close to 14 K. While this critical temperature is obviously lower than those reached in two-dimensional high-T_c cuprates, it is nevertheless higher than those of typical metallic superconductors in spite of its low carrier density. In addition, it is important to remark that this compound is the only known Cu oxide superconductor *without* two-dimensional planes. Thus, independently of whether or not this material provides a realization of the theoretical ideas based on two-leg ladders reviewed in section 2, it nevertheless provides a very interesting case for the analysis of superconductivity in Cu oxides in general.

After the report of superconductivity in doped [14–24–41], it became very important to verify that the structure at ambient pressure with clearly defined ladders and chains remains stable under the high pressure needed to induce the superconducting regime. In other words,
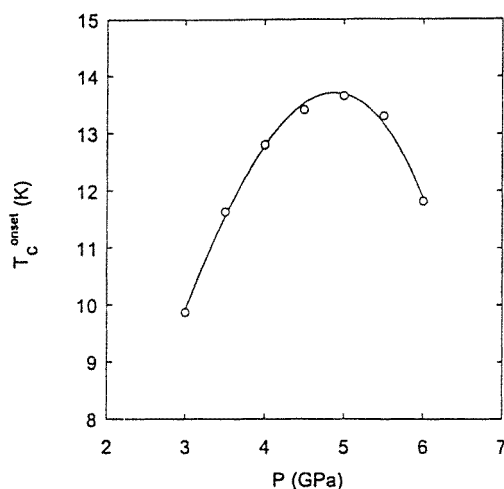
Figure 20. The temperature dependence of T_c (onset) as a function of pressure for $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41+\delta}$, reproduced from Isobe *et al* (1998).

pressure-induced structural changes could have occurred in the [14–24–41] material. This issue has been addressed recently by Isobe *et al* (1998) using x-ray diffraction measurements on a $x = 13.6$ Ca-doped sample. Among the main results reported by these authors is the confirmation that indeed no serious structural changes take place in this compound under high pressure, and as a consequence it is safe to consider that the superconducting phase is related to the original ladder–chain structure observed at ambient pressure. The main effect of pressure, apparently, is to reduce the distance between the ladders and chains (*b* direction), as the evolution of the lattice constants with pressure shown in figure 21 suggests. This result is representative of hard intraplane and soft interplane bindings. A similar conclusion is reached by analysing the effect of Ca doping upon the original Sr-based Ca-undoped phase, namely the interatomic distance ladder–chain was found to be reduced by Ca substitution (see Ohta *et al* 1997) leading to a redistribution of holes originally present only on the chains, as also discussed by Kato *et al* (1996), Motoyama *et al* (1997), Osafune *et al* (1997) and Mizuno *et al* (1997). According to Isobe *et al* (1998), the most important role of high pressure for realizing superconductivity is the hole redistribution between chains and ladders. In addition, the resistivity along the *a*-axis decreases substantially with pressure enhancing the two-dimensional characteristics of the compound, as discussed extensively below.

3.3.2. Superconductivity in doped [14–24–41] with $x = 11.5$. After the discovery of superconductivity at Ca concentration $x = 13.6$, a similar phenomenon was also observed at $x = 11.5$ by Nagata *et al* (1997). At 4.5 GPa the superconducting critical temperature at this Ca composition was found to be 6.5 K (see the inset of figure 22 for more details). Very recent specific heat and neutron scattering studies by Nagata *et al* (1998b, 1999) have found that an antiferromagnetic phase with a Néel temperature $T_N \sim 2$ K exists at this Ca composition, both at low pressures and at pressures comparable to those that induce superconductivity. Thus, in the temperature–pressure diagram antiferromagnetism and superconductivity are neighbouring phases. The discussion of the complicated spin arrangement leading to the magnetic ordering can be found in Nagata *et al* (1998b, 1999). However, since T_c is appreciably larger than T_N, it is more reasonable to continue assuming that the superconducting phase is more probably
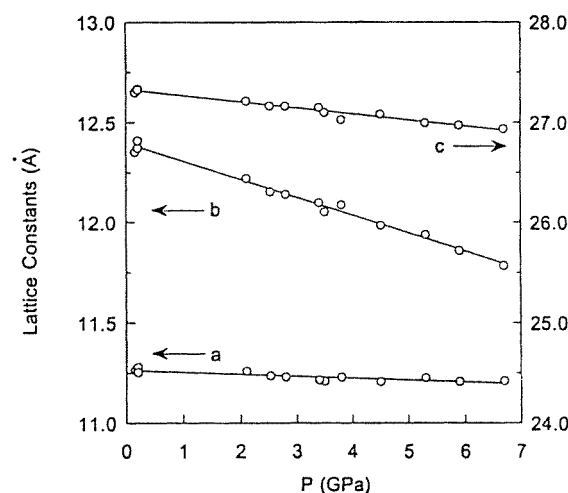
Figure 21. The pressure variation of the lattice constants of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41+\delta}$ at low temperature, reproduced from Isobe *et al* (1998). The *c*-direction runs along the legs of the ladders, *a* along its rungs, and *b* is perpendicular to both.

induced by the spin-gapped normal state that exists in these ladder materials.

In figure 22(*a*), the resistivity along the *c*-direction (legs) is shown at several pressures as a function of temperature. Indications of superconductivity below 10 K have been found in the range 3.5–8 GPa. It is interesting to note the *linear T*-dependence of ρ_c above 80 K in the ambient pressure limit, similar to that which occurs in the two-dimensional high-T_c cuprates at optimal density. This linear behaviour can also be observed within a wide range of pressures, but as the pressure increases a crossover to a T^2-dependence was found (see, for instance, the inset of figure 4 of Nagata *et al* (1998a)). Actually at 8 GPa a Fermi liquid T^2-dependent resistivity was observed between 50 and 300 K. The behaviour reported in this compound is, thus, very similar to that which occurs in the two-dimensional cuprates between the underdoped or optimal and overdoped regions. This similarity suggests that an increase of the pressure may correspond to an increase in the number of carriers on the ladder planes. The Fermi liquid behaviour at large pressure in the region where superconductivity disappears suggests that a two-dimensional Fermi liquid state is not favourable for superconductivity, as is the case in the overdoped regime of the two-dimensional high-T_c cuprates.

Nagata *et al* (1997) also reported the resistivity ρ_a in the direction perpendicular to the legs, along the ladder rungs (figure 22(*b*)). A semiconducting-like behaviour is observed below 1.5 GPa, suggesting that the charge dynamics is essentially one-dimensional and carriers are confined within each ladder. However, above this pressure the system becomes metallic. It is likely that the two-dimensional character of the electronic state increases as the interladder coupling increases due to the application of pressure. Even more illustrative is the ratio ρ_a/ρ_c versus temperature at various pressures shown in figure 23, reproduced from Nagata *et al* (1997). At low pressure this ratio can be as large as 100, while at the pressure where the superconducting volume fraction is at its maximum, ρ_a/ρ_c reaches its minimum value ~ 10. This result suggests that at low pressure the carriers are confined on ladders, similar to the way that holes are confined on the two-dimensional planes of the high-T_c cuprates, while as the pressures increases they become deconfined. However, it is somewhat surprising that at the highest pressure of 8 GPa, where the two-dimensional character should be maximized following
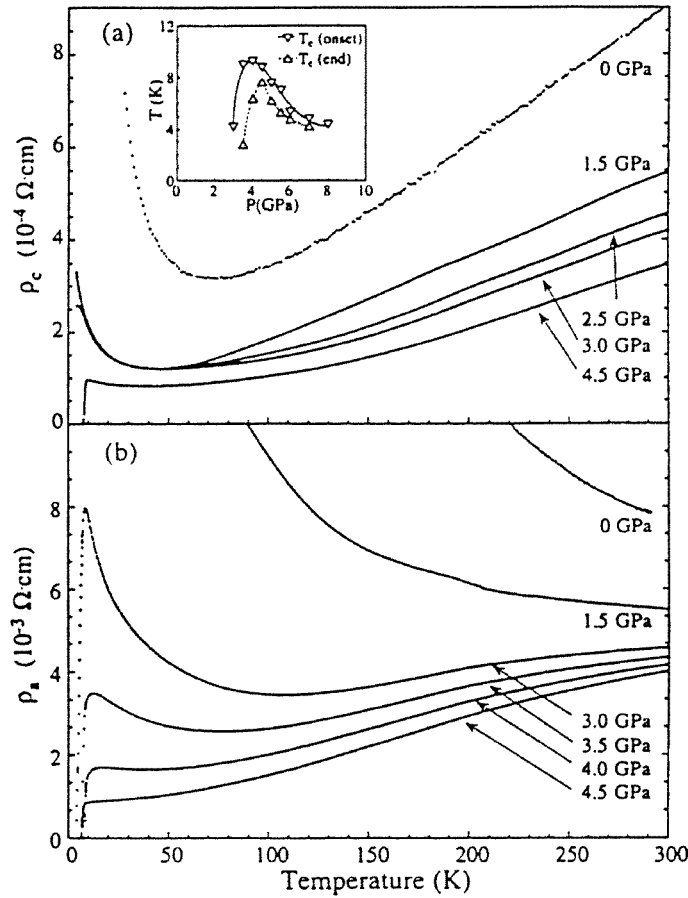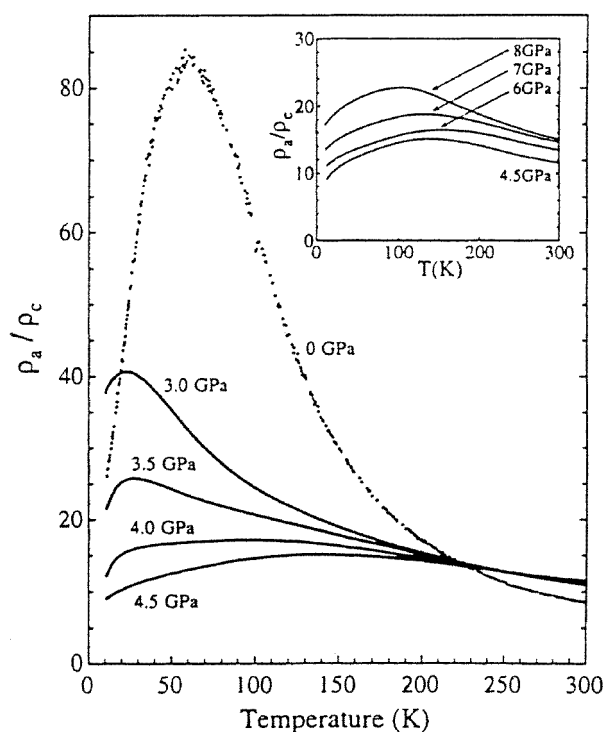
Figure 22. The effect of pressure on the temperature dependence of the resistivity (*a*) along the ladder leg direction (ρ_c) and (*b*) across the ladder rung direction (ρ_a) of single-crystal $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ at the indicated pressures. The inset shows the pressure dependence of T_c. The figure is reproduced from Nagata *et al* (1998a).

the previous reasoning, ρ_a/ρ_c is now $\sim$20, i.e. twice the minimum reached at 4.5 GPa.

It is certainly important to study the qualitative effect of pressure on the physics of the ladder compound [14–24–41]. In particular, the role of the interladder coupling in the appearance of superconductivity should be clarified. Arai and Tsunetsugu (1997) have recently estimated the interladder hopping to be 5–20% of the intraladder hopping. However, it is unclear whether this number should be considered 'small' or 'large'. It could be that under high pressure the quasi-one-dimensional charge dynamics is preserved and superconductivity develops mainly within the ladders, with a minor role played by the interladder hopping amplitude. Another possibility is that the interladder coupling, presumably enhanced as the pressure grows, induces a dimensional crossover from one to two dimensions. In this scenario, it may simply be that the ladders become an anisotropic two-dimensional Cu oxide system after the application of pressure. These issues have been recently addressed in more detail by Nagata *et al* (1998a) and the interpretation they provide of their results seem to favour the second scenario, i.e. they consider that pressure makes the [14–24–41] compound quasi-two-dimensional. They base their conclusion on the ρ_c and ρ_a resistivities shown in figure 23.

Figure 23. The effect of pressure on the temperature dependence of the anisotropic ratio ρ_a/ρ_c of single-crystal $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ at the indicated pressures. The inset shows the same anisotropic ratio but at pressures above 4.5 GPa. The figure is reproduced from Nagata *et al* (1998a).

Along the c-direction and at low temperature the system changes from an insulator to a superconductor, as was observed in two-dimensional cuprates upon Zn substitution (Fukuzumi *et al* 1996). Along the a-direction, ρ_a becomes metallic at 4.5 GPa.

Regarding the results of Nagata *et al* (1998a) this author would like to bring to the attention of the readers similar results obtained experimentally for the two-dimensional high-T_c compounds, in particular $YBa_2Cu_3O_{7-y}$. Takenaka *et al* (1994) compared the resistivity along one of the directions of the CuO planes (a-axis) against the resistivity along the direction perpendicular to the planes, which in the high-T_c cuprates is the c-axis. The results are shown in figure 24. It is important to note that near the *optimal* critical temperature, where T_c is the highest, the resistivity in *both* directions a and c is metallic. Thus, in this regime the holes seem to have been deconfined from the planes, and they can move coherently between planes. The anisotropy ρ_c/ρ_a of YBCO is shown in figure 25. Close to the optimal oxygen concentration and at 100 K this ratio is close to 50. Based on these numbers, it is difficult to avoid making a connection with the results obtained for the doped ladders. In that case, at the optimal pressure around 4.0–4.5 GPa the resistivity in both directions (along the legs and rungs of the ladders) is metallic, and the ratio ρ_c/ρ_a is between 16 and 18. The difference between 50 for optimal YBCO and 16–18 for optimal [14–24–41] does not seem particularly large. In this author's opinion, the combination of these results is suggestive of an interesting common phenomenon taking place at optimal hole concentration both in ladders and planes. The best T_c is obtained in a regime where the charge becomes deconfined to a dimension higher by one then the dimension of the dominant structure in the system, namely planes in the 2D cuprates and ladders in [14–24–41].
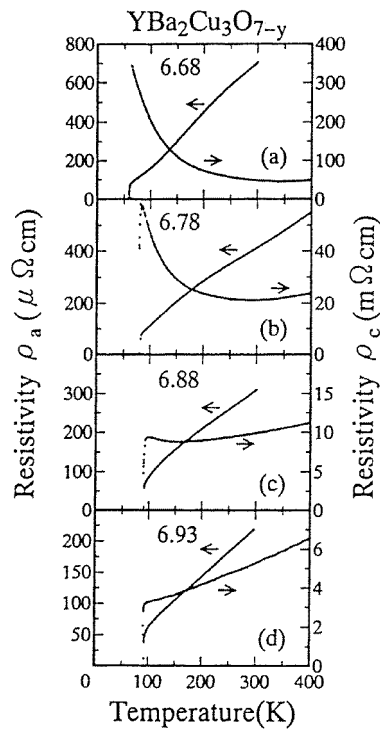
Figure 24. In-plane (ρ_a) and out-of-plane (ρ_c) resistivity of $YBa_2Cu_3O_{7-y}$ plotted as a function of temperature, reproduced from Takenaka *et al* (1994). Results are shown for various oxygen concentrations $7 - y \sim$ 6.68, 6.78, 6.88, and 6.93.
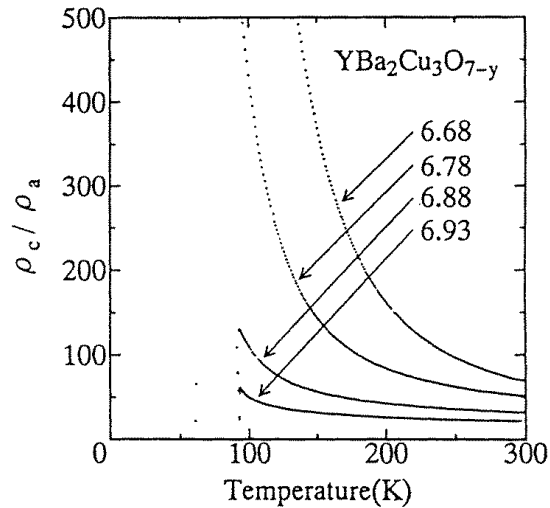
Figure 25. The anisotropic resistivity ratio ρ_c/ρ_a plotted as a function of temperature for various oxygen contents (taken from Takenaka *et al* (1994)).

If this analogy is correct, this author believes that the doped ladder compound should present an 'underpressure' or underdoped regime, with metallic behaviour along the c-axis and semiconducting at low temperature along the a-axis, before the superconducting phase is reached. Based on the recent results of Nagata *et al* (1998a), such a regime could occur at pressures below 4.0 GPa. According to Nagata *et al* (1998a) indications of superconductivity already occur at 3 GPa, and in this case the ratio ρ_a/ρ_c is 40, only about half the maximum reached at ambient pressure. Although the underdoped regime proposed here would exist, if at all, in a very narrow window in pressure, the dependence of the ladder hole concentration with such a pressure is not accurately known and it may be that changing from 3.0 to 4.0 GPa appreciably alters the number of carriers on the ladders. Of course, another possibility is an abrupt change from the insulator to an 'overdoped' superconductor as may occur in the two-dimensional electron-doped NdCeCuO high-T_c compound (S Uchida, private communication). The author believes that the study of this conjectured underdoped regime would further contribute to the understanding of the analogies and differences between the ladder and planar cuprates.

Adding to this discussion, note that even if high pressure indeed increases the two-dimensional characteristics of the system at all Ca concentrations where superconductivity is observed, the x-ray experiments of Isobe *et al* (1998) have still shown that the structure remains the same, namely with a weak interladder coupling and with nearest-neighbour ladders shifted

by half a lattice spacing. This geometry certainly does *not* correspond to a square lattice and, in addition, it is likely that the dominant physics will still arise from the individual ladders since they have the largest couplings and ρ_a/ρ_c much larger from one. In other words, if the superconductivity on ladders and two-dimensional cuprates have a common origin, any mechanism proposed for the explanation of such a phase on the square-lattice high-T_c cuprates cannot depend on the fine details of such a lattice structure since ladder compounds under pressure are also superconducting. Also, note that a competing charge-ordered state, with hole pairs as building blocks, may affect the occurrence of superconductivity at low pressure, and only at high pressure does the extra mobility in the direction perpendicular to the ladders stabilize the superconducting state, which still could occur through a pairing mechanism taking place mostly on ladders. Thus, the issue of the one- versus two-dimensional characteristics of the superconducting phase is still very much open to discussion, and this crucial issue should certainly be addressed by future experiments.

Very recently, exciting results by Balakirev *et al* (1998) have added extra evidence of an unconventional behaviour in doped ladders. These authors showed that charge transport in the non-superconducting state of $Sr_2Ca_{12}Cu_{24}O_{41}$ shares three distinct regimes in common with high-temperature superconductors, including an unexplained insulating behaviour at low temperatures in which the resistivity increases as the logarithm of the temperature. A similar regime was found previously in the two-dimensional cuprates by Ando *et al* (1995). The other two regimes correspond to a variable-range hopping behaviour at very low temperature and a linear behaviour above 150 K, as already discussed elsewhere in the text. Boebinger *et al* (1996), studying the high-T_c superconductors in pulsed high magnetic fields, found an insulator to metal crossover at low temperature in $La_{2-x}Sr_xCuO_4$. The suppression of superconductivity by the magnetic fields allowed them to analyse this insulator–metal transition below T_c. The study of the analogous metal–insulator transition in magnetic fields strong enough to suppress superconductivity for the case of two-leg ladders [14–24–41] at high pressure would be an important experiment to carry out in the near future. Its main motivation would be to find out if such a transition occurs at the optimal pressure, as happens in the two-dimensional cuprates at optimal hole density.

3.3.3. Optical conductivity $\sigma(\omega)$. The study of the possible transfer of holes from chains to ladders upon Ca doping has been illuminated by experiments reporting the optical conductivity along the *c*-axis carried out by Osafune *et al* (1997). They used single crystals of doped [14–24–41] with Ca concentration up to $x = 11$. At this hole density the *c*-axis resistivity is metallic above 80 K, while for smaller densities the system is insulating at all temperatures below 300 K. The analysis of Osafune *et al* (1997) made it possible to isolate the contributions of the ladders from those of the chains. These authors showed that holes are actually transferred from chains to ladders upon Ca substitution, as explained below. This result is in agreement with the conclusions of several other studies.

Figure 26 contains the optical conductivity along the *c*-axis obtained by Osafune *et al* (1997) for several Ca concentrations and even for a Y-doped sample ($x = 3$). It is clear from the figure that the conductivity in the low-energy region below 1.2 eV increases with x, while the charge transfer spectral weight decreases, suggesting a transfer of weight similar to that which occurs in the two-dimensional cuprates when an insulator parent compound is hole doped (see, for instance, Uchida *et al* (1991)). The analogy between results for ladders and planes clearly suggests that Ca doping produces a redistribution of holes, moving them from the chains to the ladders. If the holes were populating the chains, substantially different results would be expected instead of the observed doping of a charge transfer parent compound. In addition, the results found experimentally are similar to those found by numerical simulations of models
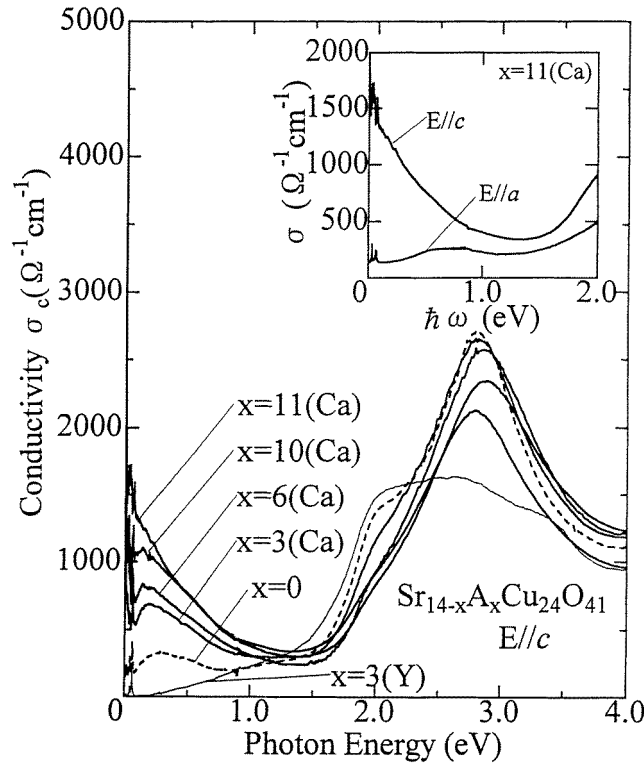
Figure 26. The c-axis optical conductivity $\sigma_c(\omega)$ of $Sr_{14-x}A_xCu_{24}O_{41}$ for various compositions. The figure is reproduced from Osafune *et al* (1997). The anisotropic spectra with a- and c-axis polarization are shown for $Sr_3Ca_{11}Cu_{24}O_{41}$ in the inset.

for ladders by Hayward *et al* (1996b). The low-energy integrated optical conductivity up to ω, namely $N_{eff}(\omega)$, is shown in figure 27, and it also resembles results for the two-dimensional cuprates. Based on these analogies, Osafune *et al* (1997) estimated the concentration of holes on the ladders as a function of Ca doping. The result is shown in the inset of figure 27. At $x = 11$, the nominal valence of Cu is 2.2, which corresponds to 0.2 holes per Cu on the ladders. Once again, these doping concentrations resemble those reached in the two-dimensional square lattice cuprates.

Interesting recent results by Osafune *et al* (1999) using optical techniques have contributed further to the understanding of doped ladder materials. These authors concentrated their efforts on the infrared part of the spectra of single crystals [14–24–41] with $x = 8$ and 11, as representatives of the low- and high-doping regions of the ladders (having 0.16 and 0.20 holes per ladder-Cu, respectively, based on the previous analysis of Osafune *et al* (1997)). The resistivity along the leg (c) and rung (a) directions is shown in figure 28. At $x = 8$ both directions show an insulating-like behaviour, while at $x = 11$ there is a range of temperatures where the system is metallic in the leg direction and insulating in the rung direction. An interesting feature in the a-axis optical conductivity $\sigma_a(\omega)$ both at $x = 8$ and 11 is shown in figure 29. A pseudogap in the low-frequency region appears upon lowering the temperature (see also Ruzicka *et al* 1998). It is reasonable to expect that the insulating properties that exist in ρ_a versus T are related with this pseudogap, as occurs in underdoped high-T_c cuprates when the pseudogap and resistivity in the interplane direction are contrasted (see Homes *et al* 1993).
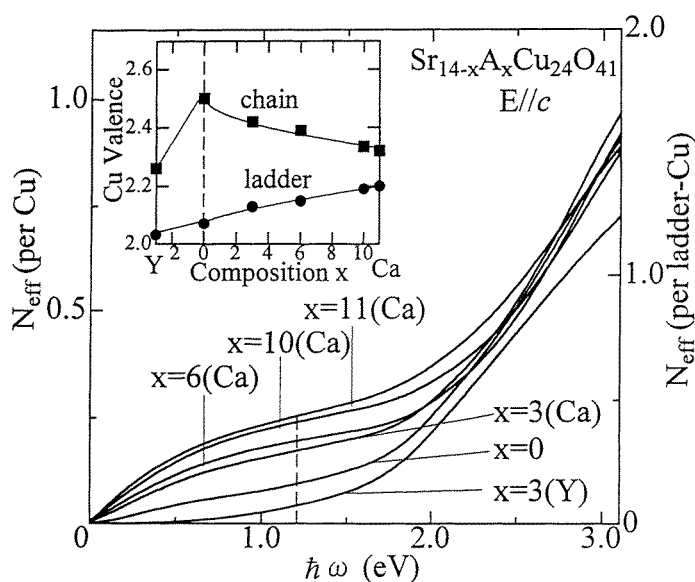
Figure 27. The effective electron number N_{eff} per Cu (left-hand scale) presented as a function of energy for various compositions. The valences of both chain- and ladder-Cu estimated for each composition are plotted in the inset. Details can be found in Osafune *et al* (1997).

In addition, the NMR experiments of Magishi *et al* (1998) showed that the temperature T^* at which a gap opens in the doped ladders coincides with the analogous temperature arising from $\rho_a(T)$ data.

In contrast to the pseudogap in the *a*-direction, the *c*-axis optical conductivity $\sigma_c(\omega)$ was found by Osafune *et al* (1999) to be dominated by a low-frequency peak which rapidly grows with lowering temperature (figure 30). This is not a Drude peak since it is located at a finite frequency: $\sim$100 cm^{-1} and $\sim$50 cm^{-1} for $x = 8$ and 11, respectively. Osafune *et al* (1999) have interpreted this result as arising from a charge density wave (CDW) mode of hole pairs. In addition, independent studies of the electrodynamics of $x = 0, 5$, and 12 [14–24–41] samples by Ruzicka *et al* (1998) led to a similar proposal of a CDW of hole pairs at low temperatures. Pseudogap features along the *c*- and *a*-axis were also observed by these authors. Also, Owens *et al* (1996) using microwave loss measurements detected superconductive pairing fluctuations close to a CDW instability. The proposed hole pair CDW state is certainly possible since it is well known from theoretical calculations that superconductivity and charge ordering are competing states in many models (see Dagotto *et al* 1992, Noack *et al* 1994 and Tsunetsugu *et al* 1995). Indeed, the effective mass that Osafune *et al* (1999) obtained from their analysis is very largely suggestive of the collective nature of the excitation. Thus, the proposed picture is that hole pairs are formed and confined on the ladders, as predicted by theory, at small hole concentration. As the hole density grows they seem to form a CDW state of pairs. Upon increasing the hole concentration and working at intermediate temperatures the CDW may be depinned by thermal fluctuations and both pairs and single holes could contribute to the resistivity along the *c*-axis. Needless to say, it is very important to extend these results obtained at ambient pressure into the superconducting regime at high pressure, where both resistivities indicate a metallic behaviour. Finally, note that very recent Cu NQR and NMR experiments by Ohsugi *et al* (1999) for the Ca ($x = 11.5$) ladder have revealed three-dimensional magnetic ordering below $T_N = 2.2$ K, with small moments appearing on the ladders and large moments
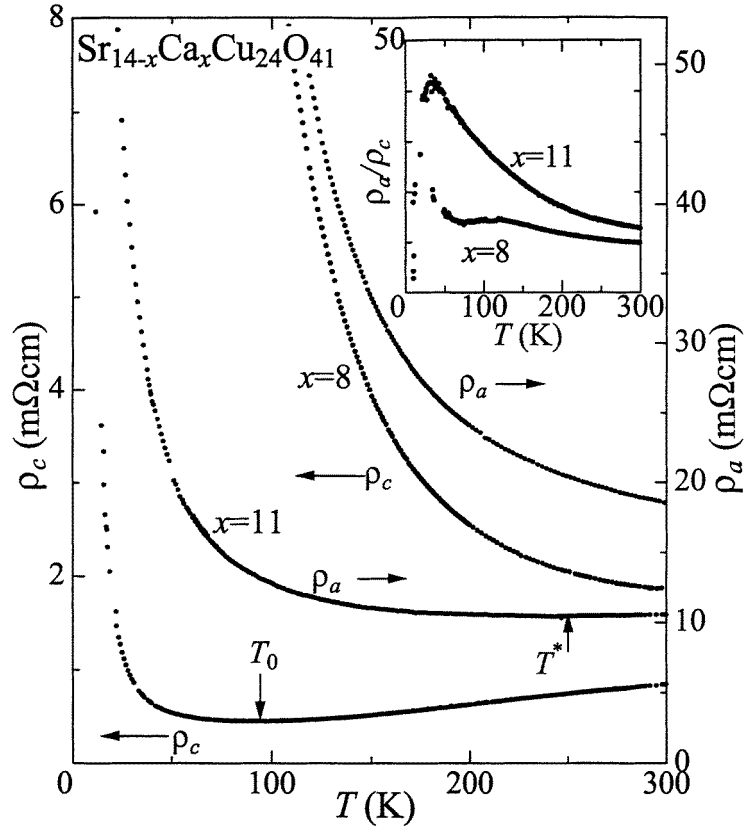
Figure 28. The T-dependence of the resistivities along the legs (ρ_c) and rungs (ρ_a) of the ladders in the compound $Sr_{14-x}Ca_xCu_{24}O_{41}$, with $x = 8$ and 11 (taken from Osafune *et al* (1999)). The temperatures T^* and T_0 where $d\rho/dT$ changes sign are indicated for $x = 11$. The anisotropic resistivity ρ_a/ρ_c versus temperature is plotted in the inset.

on the chains. It was suggested that the CDW state of pairs plays an essential role in stabilizing the magnetic state.

3.3.4. NMR. A comprehensive Cu NMR study of single crystals of $Sr_{14-x}Ca_xCu_{24}O_{41}$ has been recently reported by Magishi *et al* (1998). These authors analysed the ^{63}Cu NMR spectrum, Knight shift, nuclear spin lattice relaxation rate $1/T_1$, and the spin echo decay rate $1/T_{2G}$ for samples with $x = 0, 6, 9,$ and 11.5. The main reported results emerging from this study are the following:

(i) Through the Knight shift and $1/T_1$ measurements, the spin gap was inferred. The analysis of both quantities suggest that the gap decreases as the Ca concentration grows (see figure 31). Qualitatively similar results were found using polycrystals by Tsuji *et al* (1996).

(ii) In particular, for $x = 11.5$ and ambient pressure the gap was found to be finite and approximately 300 K (from Knight shift the result is actually 270 K, while from $1/T_1$ it is 350 K). This is important since at this Ca concentration superconductivity has been observed upon the application of pressure by Nagata *et al* (1997). Figure 32 shows the
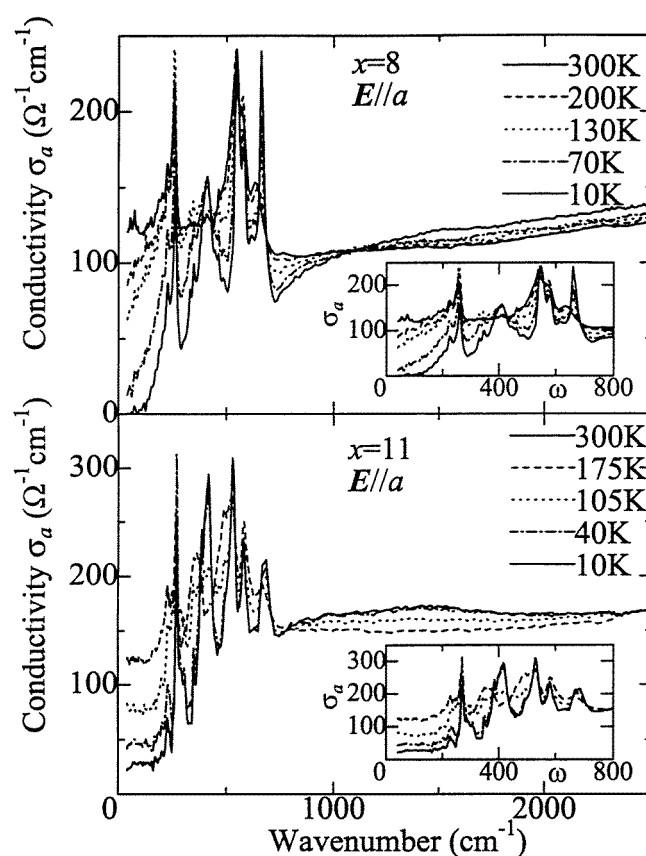
Figure 29. The a-axis optical conductivity spectra $\sigma_a(\omega)$ below 2500 cm^{-1} at various temperatures are shown for $x = 8$ (upper panel) and 11 (lower panel) (taken from Osafune *et al* (1999)). In the insets are shown the spectra below 800 cm^{-1} to show the redistribution of the oscillator strength of the phonons.

overall phase diagram obtained using NMR techniques. Note that the spin gap seems to flatten as x continues growing, and it becomes unclear at what Ca composition the gap will finally vanish if at all. The flattening of the spin gap with Ca composition is actually in contradiction to the previous results of Kumagai *et al* (1997) using polycrystals. Note that in spite of the presence of a nearly constant spin gap at large x, the conductivity changes substantially with increasing Ca concentration.

(iii) From data corresponding to T_{2G}, the spin correlation length ξ was obtained experimentally. It was found to decrease as x grows, as expected. Assuming this length is dominated by the mean distance among mobile holes, at Ca-11.5 a hole concentration of $x = 0.25$ holes per Cu_2O_3 was obtained. This value is in good agreement with the hole concentration $x = 0.22$ inferred from optical measurements by Osafune *et al* (1997).

(iv) At a temperature of around 60 K, charge localization takes place. The resistivity increases in this regime.

(v) The resistivity has a very interesting behaviour with temperature as already discussed elsewhere in this review. At 'high' temperatures the resistivity along the c-axis (i.e. along the legs of the ladders) is linear, while in the perpendicular direction the resistivity is
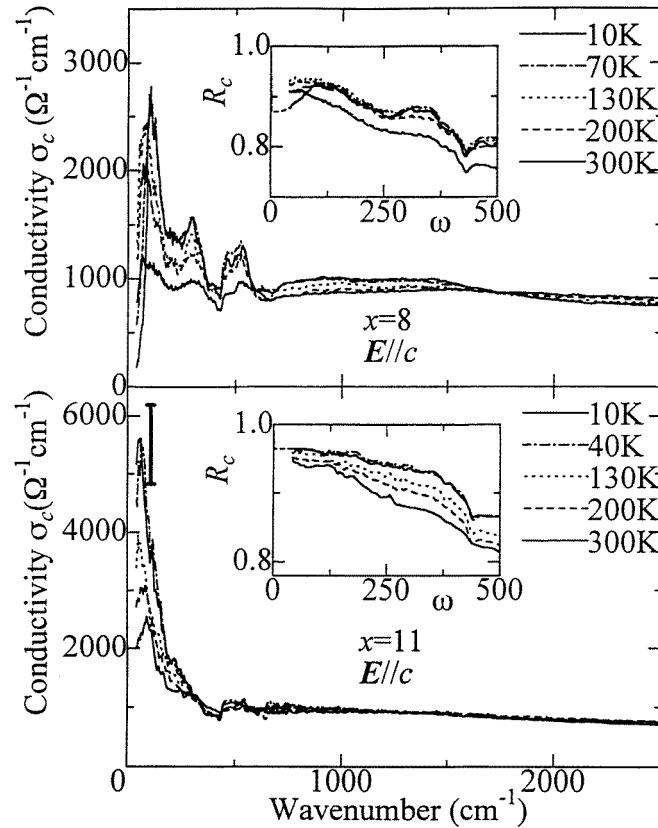
Figure 30. The c-axis optical conductivity spectra $\sigma_c(\omega)$ at various temperatures for $x = 8$ (upper panel) and 11 (lower panel). The optical reflectivity spectra in the low-frequency region are shown in each inset. This figure is from Osafune *et al* (1999), which should be consulted for further details.

T-independent and larger by an order of magnitude. The spin dynamics was found to be consistent with the $S = \frac{1}{2}$ one-dimensional Heisenberg model. In an intermediate temperature regime the resistivity deviates slightly from the linear T-dependence, again similarly to the two-dimensional doped cuprates in the pseudogap region, while ρ_a grows as T decreases. These results suggest that in this regime pairs are expected to be formed, but they are confined into the ladders. In the 'low' temperature regime, charge localization presumably takes place through the localization of the hole pairs on the ladders. In order to understand whether or not the application of pressure deconfines the hole pairs from the ladders, NMR studies should be carried out in the regime of high pressure, and some results are already available, as discussed below.

Several other NMR experiments on ladder materials have also been reported. They include Cu NQR measurements for $Sr_{14}Cu_{24}O_{41}$ by Carretta *et al* (1998), and ^{17}O NMR in doped and undoped $A_{14}Cu_{24}O_{41}$ ($A_{14} = La_6Ca_8$, $Sr_{11}Ca_3$) by Imai *et al* (1998). A comprehensive $^{63,65}Cu$ NMR/NQR study by Takigawa *et al* (1998) on single crystals of undoped 14–24–41 reported two distinct resonance spectra for the chains, assigned to magnetic Cu sites and nonmagnetic Zhang–Rice singlets. Microwave frequency studies of the dynamical magnetic susceptibility by Zhai *et al* (1999) show indications of charge ordering in the doped 14–24–41 material.
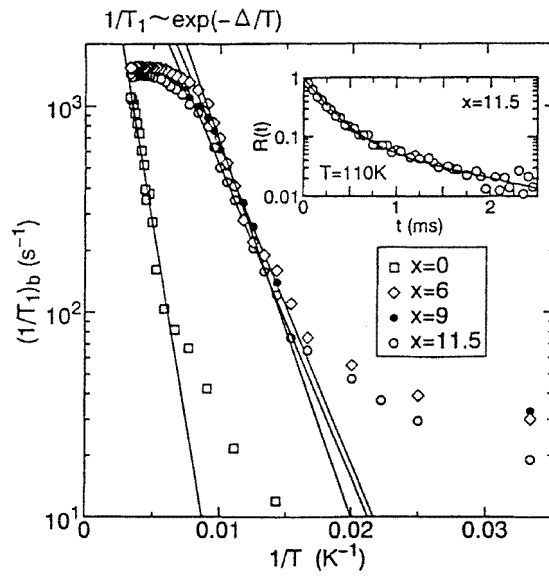
Figure 31. $(1/T_1)_b$ for a magnetic field parallel to the b-axis versus $1/T$. Results are shown for several Ca compositions of $Sr_{14-x}Ca_xCu_{24}O_{41}$. The solid lines are fits to $1/T_1 \sim \exp(-\Delta/T)$. The inset contains the relaxation function of the nuclear magnetization at $T = 110$ K in Ca-11.5. The figure is reproduced from Magishi *et al* (1998).
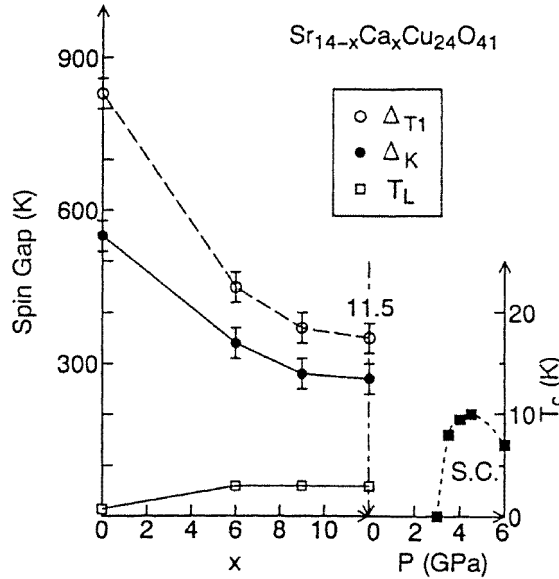
Figure 32. Spin gap versus the amount of Ca substitution in $Sr_{14-x}Ca_xCu_{24}O_{41}$, reproduced from Magishi *et al* (1998). Also shown is T_c versus pressure at $x = 11.5$. The spin gaps Δ_K and Δ_{T_1} are obtained from the Knight shift and T_1, respectively. T_L is the temperature associated with the localization of pairs. For more details see Magishi *et al* (1998).

More recently, Mayaffre *et al* (1998) reported [63]Cu NMR measurements of the Knight shift and relaxation time T_1 on the $x = 12$ Ca-doped [14–24–41] compound at high pressure. When the system becomes superconducting at 5 K and 31 kbar, those authors argued that the spin gap collapsed based on, e.g., the relaxation rate T_1^{-1} versus temperature data shown in figure 33. In addition, since they observe that superconductivity starts when the ladder spin gap collapses, they argue that the ladder is responsible for the superconducting phase. It may be that the preformed pairs on the two-leg ladders become dissociated upon pressure, making possible the hole hopping in the direction perpendicular to the legs. Regarding this interesting NMR data by Mayaffre *et al* (1998), this author believes that it is important to obtain an independent confirmation of such an important result. Very recently, Mito *et al*
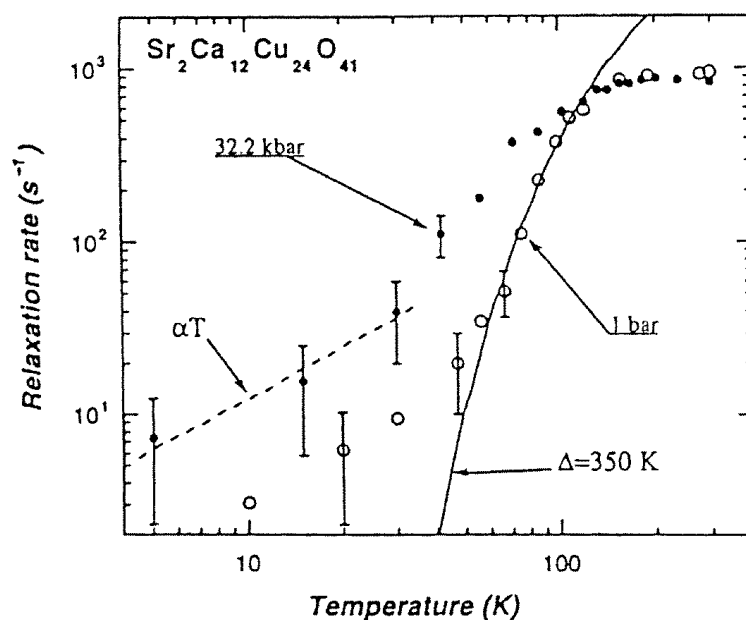
Figure 33. The temperature dependence of the ^{63}Cu ladder relaxation rate T_1^{-1} at 1 bar and 32.2 kbar. The figure is reproduced from Mayaffre *et al* (1998).

(1998) once again using NMR techniques at high pressure for a single crystal of [14–24–41] with $x = 12$ studied the Knight shift and T_1 versus temperature up to pressures 1.7 GPa. They found a robust spin gap in their studies of magnitude quite similar to the result obtained at ambient pressure. It is difficult to understand how this gap can disappear so abruptly as the pressure goes up to 3 GPa, as claimed by Mayaffree *et al* (1998). Hopefully Mito *et al* will be able to extend their analysis to higher pressures in the near future. In addition, it should be investigated to what extent the collapse of the spin gap reported by Mayaffre *et al* (1998) corresponds to the creation of a small population of low-energy excitations by pressure, leaving large weight at the original spin gap position which may remain mostly untouched as a high-energy feature, as has been shown theoretically to occur in the t–J model for two-leg ladders doped with vacancies by Martins *et al* (1996, 1997). In other words, it would be interesting to investigate if the results of Mayaffre *et al* (1998) correspond to the replacement of a hard gap by a 'pseudogap', namely a clear depletion in the spin density of states at low-energy which, however, does not vanish at any finite energy. Such a behaviour is known to occur in the high-temperature superconductors, and it would be very important to analyse to what extent doped ladders present a similar pseudogap phenomenology. Actually, very recent NMR experiments by Auban-Senzier *et al* (1999) already support the conjecture discussed here that a pseudogap appears in doped ladders at the high pressures needed to reach the superconducting state.

3.3.5. Inelastic neutron scattering.   Inelastic neutron scattering (INS) experiments on the [14–24–41] compound have also been reported. Using this technique, Eccleston *et al* (1996) analysed a polycrystalline sample of $x = 2.8$ [14–24–41] and they observed a gap of 35 meV for the ladder. Broad features at 10 meV corresponding to chain excitations were also reported. More recently, Eccleston *et al* (1998) presented the first INS study which has been able to access the spin ladder excitations using single crystals of a cuprate ladder material. A ladder spin
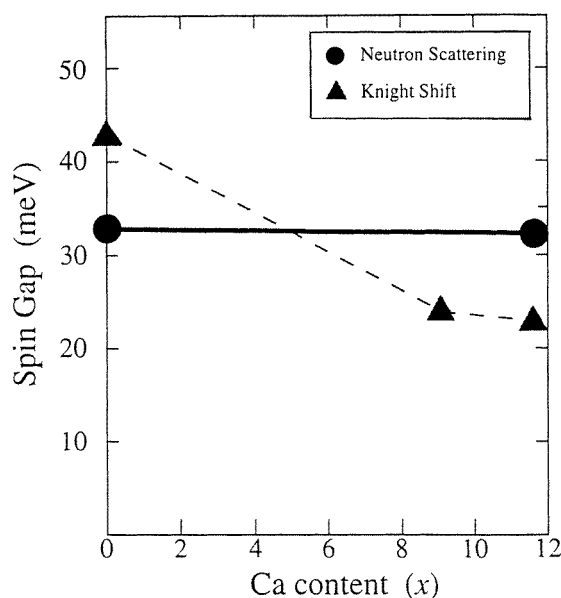
Figure 34. Spin gap as a function of Ca content in [14–24–41] at ambient pressure. The circles show the results from neutron scattering experiments (Katano *et al* 1999). The triangles are the results from the Knight shift in the NMR experiments of Magishi *et al* (1998). The figure is reproduced from Katano *et al* (1999).

gap of 32.5 ± 0.1 meV was reported with the scattering function $S(q, \omega)$ sharply peaked about the antiferromagnetic zone centre. A band maximum at 193.5 ± 2.4 meV was also observed. Excitations at energy transfers of 15 meV or below were assigned to the chains present in [14–24–41]. INS results with emphasis on the physics of chains have also been reported recently by Regnault *et al* (1998) and Matsuda *et al* (1998), adding to the studies of Hiroi *et al* (1996), Matsuda *et al* (1996, 1997), Cox *et al* (1998), and others who have concentrated their efforts on the analysis of that portion of the structure of [14–24–41]. The rich physics of dimerized chains observed in this compound will not be reviewed here since the focus of the paper is on the physics of ladders, but it is clear that its analysis deserves further attention.

Recent inelastic neutron scattering results by Katano *et al* (1999) for a single crystal of $x = 11.5$ [14–24–41] at both ambient pressure and high pressure of 0.72, 2.1 and 3.0 GPa produced surprising conclusions. Contrary to the NMR results of Magishi *et al* (1998), Katano *et al* (1999) reported a spin gap in the doped system which does *not* change from that of the parent material. This occurs even under high pressure. The origin of these differences between NMR and INS is unclear at present (see figure 34). Note that for $x = 11.5$ in the [14–24–41] material superconductivity appears between 3.5 and 8 GPa, i.e. very close in pressure values to the last set of experiments by Katano *et al* (1999). Note also that the INS data, if valid at slightly larger densities, would be in contradiction with the results of Mayaffre *et al* (1998) that reported the absence of a spin gap in the $x = 12$ [14–24–41] compound under 3.2 GPa of pressure. This author would like to remark that the analysis of the pressure dependence of the INS data into the pressure range of the superconducting state is very important, it should certainly continue, and further work will hopefully resolve the discrepancy between INS and NMR results.
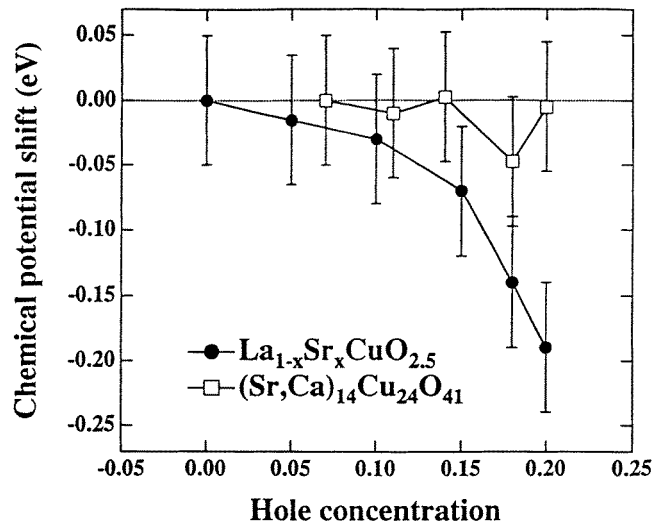
Figure 35. Chemical potential shift as a function of hole concentration of the Cu–O ladder for $(La, Sr, Ca)_{14}Cu_{24}O_{41}$ compared with that for $(La, Sr)CuO_{2.5}$. These results are reproduced from Mizokawa *et al* (1998). The hole concentration of the ladder has been taken from the optical study of Osafune *et al* (1997).

3.3.6.   Photoemission and angle-resolved photoemission $A(p, \omega)$.   Angle-resolved photoemission studies of the ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ have been carried out by Takahashi *et al* (1997) and Sato *et al* (1997) using single crystals with $x = 0$ and 9. These authors found two dispersive features in their data. One has an energy dispersion of about 0.5 eV, matching well the periodicity of the ladder. The minimum binding energy is located at momentum $ka = \pi/2$ for $x = 0$, in rough agreement with numerical studies of the $t–J$ model by Tsunetsugu *et al* (1994, 1995), Troyer *et al* (1996), Haas and Dagotto (1996) and Martins *et al* (1999), that locate this minimum close to, although not exactly at, $\pi/2$ in the bonding band of isolated ladders. The other features in the photoemission results by Takahashi *et al* (1997) are deeper in energy, and they seem to correspond to chain excitations.

Other studies of the electronic structure of $(La, Sr, Ca)_{14}Cu_{24}O_{41}$ using core-level photoemission spectroscopy have been presented by Mizokawa *et al* (1998), and the results compared with another ladder compound, $La_{1-x}Sr_xCuO_{2.5}$, as well as the high-T_c material $La_{2-x}Sr_xCuO_4$. These authors observed that the chemical potential shift in doped [14–24–41] is considerably suppressed compared with the other two compounds, as shown in figure 35. Mizokawa *et al* (1998) interpreted this as an indication of a non-Fermi liquid state on the [14–24–41] ladders being more robust against hole doping than in other Cu oxides.

This interesting result shows that much remains to be learned about ladders using photoemission experiments and hopefully in the future information as rich as reported for the high-T_c compounds will be also available for ladders. In this context, theory is still ahead of experiments and a considerable amount of information is already available to contrast experiments with results for the $t–J$ model (see, for instance, Riera *et al* (1999)). In particular, Martins *et al* (1999), using a novel technique that allowed them to study clusters containing 2×20 sites, recently reported the evolution with doping of the dominant peak in the one-particle spectral function $A(q, \omega)$, presumed to be a quasiparticle, as a function of density. The result is shown in figure 36 for the bonding band $q_y = 0$. At $x = 0.0$ (undoped limit) the bonding band is very narrow. At $x = 0.125$, it remains flat near $(\pi, 0)$, similar to its behaviour
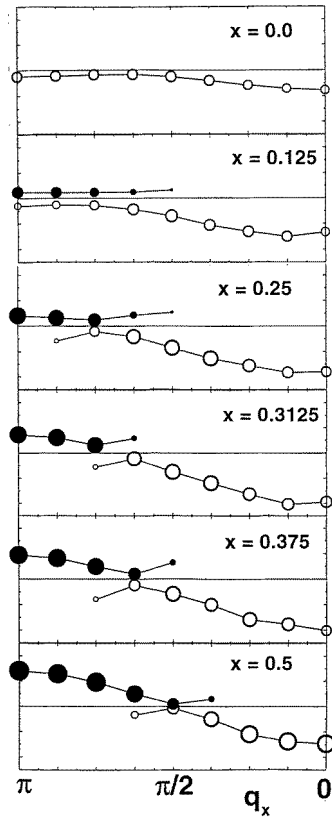
Figure 36. The dominant peak in the one-particle spectral function $A(p, \omega)$ obtained numerically using the t–J model, parametric with hole density x. The coupling used was $J/t = 0.4$ and the lattice had up to 2×20 sites. The size of the points is proportional to the intensity of the peak. Open circles correspond to photoemission, while full circles are in the inverse-photoemission region. The figure is taken from Martins *et al* (1999), where more details about the calculation can be found.
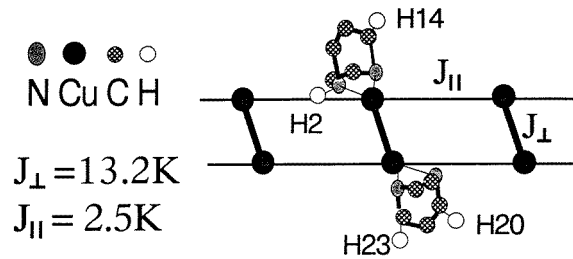
Figure 37. Schematic structure of $Cu_2(C_5H_{12}N_2)_2Cl_4$. The labelled protons contribute to the NMR lines study, as discussed by Chaboussant *et al* (1997b).

in experiments for the two-dimensional cuprates. A gap develops at this density due to pair formation. As x keeps on growing the photoemission and inverse-photoemission bands lose their flatness and start deforming, resembling more a quasi-non-interacting dispersion which is reached at $x = 0.5$. This theoretical result is the first one available where the evolution of the one-particle spectral function with doping has been reported between a limit dominated by short-range antiferromagnetic correlations and a quasi-non-interacting regime. The analogous result for the two-dimensional cuprates is still unknown.

3.4. The strong-coupling ladder compound $Cu_2(C_5H_{12}N_2)_2Cl_4$

Spin ladders belonging to the organic family of materials have also been synthesized. In particular, the compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ has Cu ions which are coupled antiferromagnetically in isolated ladders, as remarked by Chaboussant *et al* (1997a, b). The schematic structure of this compound is shown in figure 37. The coupling between coppers is mediated by chlorine ions (not shown in figure 37). The orbitals involved in the process have a small overlap producing a reduced value for that coupling. Experimentally, the Heisenberg exchanges were found to be $J_\perp = 13.2$ K and $J_\parallel = 2.4$ K, following the notation of figure 37, leading to an anisotropic ladder that belongs to the strong-coupling limit since $J_\perp/J_\parallel = 5.5$ (Chaboussant *et al* 1997b). In this case, the rung spin singlet must be very strong, leading to a regime which is under good control in the theoretical calculations using t–J-like models. The physics in this strong-coupling region of parameter space is expected to be smoothly connected to the isotropic regime $J_\perp \sim J_\parallel$, as discussed in section 2 and by Dagotto *et al* (1992). In addition, the intrinsic small values of the Heisenberg couplings allow for investigations in static magnetic fields of comparable strength, providing a window of research that is not possible in the inorganic cuprate ladders with exchange couplings of order 0.1 eV $\sim$ 1000 K. Since at large $J_\perp/J_\parallel$ the dominant spin configurations are singlets along the rungs, the lowest-energy excitations correspond to local rung triplets which can move along the ladder. A finite density of these excitations is needed to represent the physics of ladders in high magnetic fields of strength large enough to produce a finite magnetization.

After NMR techniques were applied to the organic ladder compound by Chaboussant *et al* (1997b), a spin gap $\Delta \sim J_\perp - J_\parallel$ was reported, in agreement with theoretical expectations at large $J_\perp/J_\parallel$. In addition, the gap obtained from the static susceptibility χ and the dynamical spin structure factor obtained from the NMR measurements were found to be identical, as predicted by theory. Further work by Chaboussant *et al* (1998a), still using NMR methods, analysed the transition from the gapped spin liquid state to a gapless magnetic regime. At the critical magnetic field $H_{c1} \sim 7.5T$ where the gap closes, the system is in a quantum critical regime where the temperature is the only relevant scale. At a larger field, H_{c2}, the system becomes fully polarized. Measurements of the susceptibility and magnetization in this regime are in good agreement with calculations by Weihong *et al* (1997) (see also Hayward *et al* 1996a). More recent studies of the organic ladder by Calemczuk *et al* (1999), based on specific heat data, reported a possible incommensurate gapped state due to a small magneto-elastic coupling of the isolated ladders with the three-dimensional lattice. Associating the rung singlet and rung triplet states, the latter having spin projection along the magnetic field, with fictitious 'spin' states up and down, Chaboussant *et al* (1998b) argued that the physics of strongly coupled ladders in high magnetic fields can be mapped into a one-dimensional XXZ Heisenberg spin model which is known from previous investigations to present incommensurate phases in magnetic fields. Calculating the magnetization with the Bethe ansatz applied to the XXZ model and comparing the results with the experimental magnetization leads to an excellent agreement (see figure 38). Since the XXZ model is equivalent to spinless fermions which in one-dimensional form Luttinger liquid (LL) states, a regime with these characteristics was conjectured to exist between H_{c1} and H_{c2}, as indicated in figure 39. At very low temperatures the small couplings between ladders will destabilize the LL leading to a charge-ordered state, as also shown in figure 39.

Other recent developments in this context include the presence of plateaux in the magnetization curve in the vicinity of $(H_{c1} + H_{c2})/2$, as argued by Cabra *et al* (1997), Cabra and Grynberg (1998) and others. Calculations for coupled ladders in a magnetic field have also been recently reported by Giamarchi and Tsvelik (1998). Other studies in magnetic fields
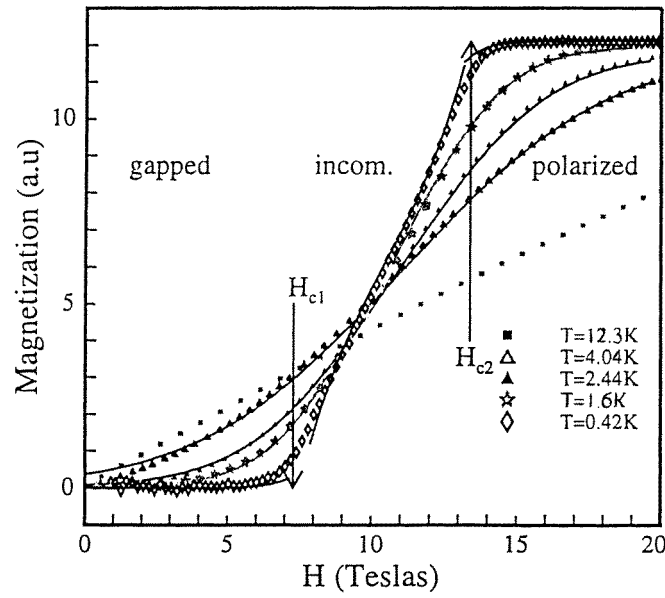
Figure 38. Magnetization of $Cu_2(C_5H_{12}N_2)_2Cl_4$ between 0 and 20 T, at different temperatures, reproduced from Chaboussant *et al* (1998b). The symbols are experimental data points, while the solid curves are the fits to the XXZ model (for details, see the text and Chaboussant *et al* (1998b)). The critical fields are indicated.
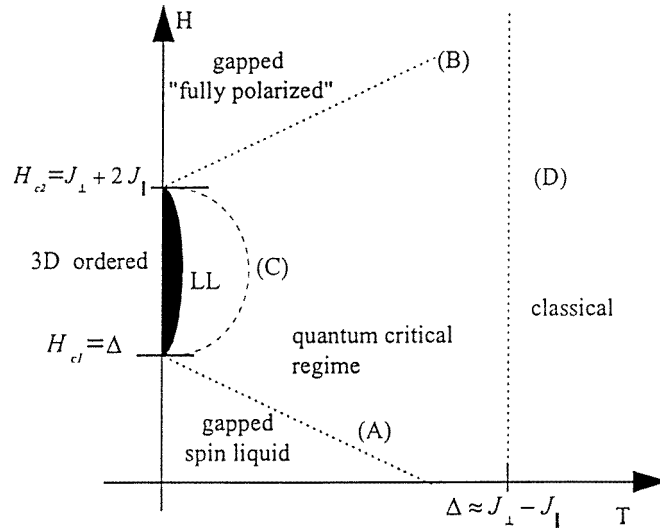
Figure 39. Phase diagram of spin ladders in a magnetic field, reproduced from Chaboussant *et al* (1998b). The quantum critical regime at finite temperature above H_{c1} is shown. The 'LL' label corresponds to a possible Luttinger liquid region. Further details can be found in Chaboussant *et al* (1998b).

were presented by Schmeltzer and Bishop (1998). In addition, some of the results derived in terms of a ladder with only two couplings ($J_\perp, J_\parallel$) are controversial since Hammar *et al* (1998) argued that extra ladder couplings, as well as multimagnon excitations and interladder
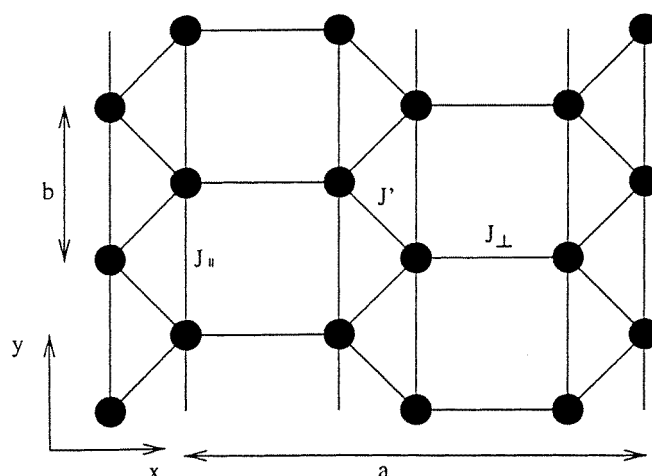
Figure 40. Schematic representation of the trellis lattice corresponding to the structure of the vanadates, reproduced from Miyahara *et al* (1998). The full circles are the positions of the V ions. The oxygens in between are not shown. The couplings that are shown correspond to the Heisenberg exchange constants used to model the behaviour of this material.

couplings, may be needed to properly reproduce their inelastic neutron scattering and specific heat data (see also Hayward *et al* 1996b). Overall, it is clear that the analysis of ladder systems under high magnetic fields have already revealed an unexpectedly rich structure, and theoretical and experimental efforts should continue exploring this interesting regime in parameter space.

Finally, doping with impurities the organic ladder can reveal interesting physics. Using computational techniques, Laukamp *et al* (1998) predicted that Zn doping of the organic strong-coupling ladder should not produce important changes in the spin gap, contrary to what is observed in other Zn-doped ladders. Experiments are already in agreement with this prediction (see Deguchi *et al* 1998).

3.5. Vanadium-based ladder compound CaV_2O_5

Interesting studies by Iwase *et al* (1996) showed that the vanadate CaV_2O_5 has a large spin gap of about 500 K. The structure of this compound corresponds to a depleted two-dimensional square lattice. It consists of a so-called trellis lattice with two-leg ladders containing V ions in a V^{4+} state of spin-$\frac{1}{2}$, with the idealized structure shown in figure 40. The ladders are coupled through 90° oxygen bonds which are expected to produce a weak exchange, a geometry similar to that in some of the cuprate ladder materials, although involving the vanadium d_{xy} orbitals. Actually, studies by Normand *et al* (1997) reported couplings $J_\perp/J_\parallel \sim 4.3$ and $J_\parallel/J' \sim 3.5$, in the notation of figure 40. However, recent quantum Monte Carlo simulations of the trellis lattice Heisenberg model by Miyahara *et al* (1998) produced a magnetic susceptibility versus temperature in agreement with experiments if $J_\perp \sim 670$ K, $J_\parallel \sim 67$ K, and $J' \sim 45$ K, namely using $J_\parallel \sim J'$. This result suggests that the dominant structures in the vanadate ladders are the dimers or rungs with spins coupled by $J_\perp$, rather than the ladders themselves. The resolution of this discrepancy is important, to decide whether or not CaV_2O_5 should be considered as a two-leg ladder material.

More recently, the compound MgV_2O_5 has also been studied (see Millet *et al* 1998). The V oxide planes of this material are very similar to those of CaV_2O_5. However, the observed

a-axis

● Cu^{2+} ○ Cl$^-$
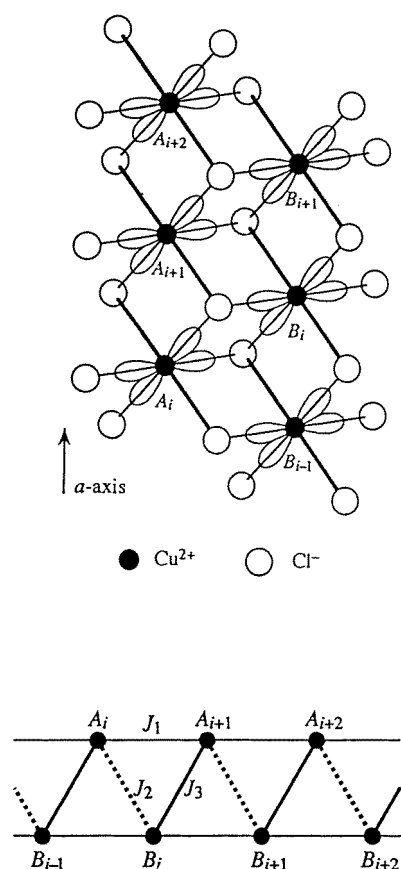
Figure 41. The double chain structure in KCuCl$_3$ and the configuration of the hole orbital d($x^2 - y^2$) of the Cu^{2+} ion are shown in the upper panel. Filled and open circles are Cu^{2+} and Cl$^-$ ions, respectively. In the lower panel, the structure of the exchange interactions expected in the present system is shown. The figure is reproduced from Tanaka *et al* (1996).

gap is just 15 K, much smaller than the 500 K reported for the latter. The difference was explained by Millet *et al* (1998) on the basis of a frustrated coupled ladder model. Other recent developments involve the spin-Peierls compound NaV$_2$O$_5$. Based on the determination of the crystal structure of this compound by x-ray diffraction and on density-functional calculations, Smolinski *et al* (1998) argued that NaV$_2$O$_5$ can be considered a quarter-filled two-leg ladder system. The exchange interaction of NaV$_2$O$_5$ across the rungs was found to be larger than along the legs by a factor of five. Since this compound and CaV$_2$O$_5$ are isostructural, it was argued that the latter should also be regarded as a (half-filled) ladder system instead of only having isolated dimers (see the discussion above). Very recent results by Lemmens *et al* (1998) using Raman scattering applied to NaV$_2$O$_5$ showed an interesting sequence of magnetic bound states at low temperatures. The importance of doping NaV$_2$O$_5$ away from quarter-filling was remarked by Smolinski *et al* (1998). Clearly this system provides a new playground to test the interplay between spin, charge, orbital and lattice degrees of freedom in a ladder geometry, and further work should be pursued in this context.

3.6. The ladder compound $KCuCl_3$

Recently, Tanaka *et al* (1996) have presented interesting arguments suggesting that the material KCuCl$_3$ can also be described as a double spin chain system. The crystal structure of this compound is shown in figure 41. The main feature is the double chain of edge-sharing CuCl$_6$

octahedra along the *a*-axis. Also in figure 41 is shown the expected pattern of Heisenberg exchange couplings arising from such a structure. They involve not only the standard rung and leg couplings, but also a plaquette diagonal coupling. Their values are expected to be small since $\sim 90°$ bonds are involved in the structure. To investigate the nature of the ground state of this material, Tanaka *et al* (1996) studied the temperature dependence of the magnetic susceptibility. The low-temperature results can be fit very well with the formula $\chi \sim (1/\sqrt{T}) \exp(-\Delta/k_B T)$ proposed by Troyer *et al* (1994). The gap obtained by this procedure was found to be 35 K. Large-scale quantum Monte Carlo calculations performed by Nakamura and Okamoto (1998) on the spin model believed to describe this material found an agreement with the experimental data within 1% relative errors in the full range of temperatures investigated. The theory–experiment comparison involved neutron scattering data obtained by Kato *et al* (1998). The couplings that reproduce the experimental data the best are $J_1 = 12.3$ K, $J_2 = 4J_1$ and $J_3 \sim 0$, suggesting that the extra coupling J_3 may not be necessary. In addition, note that related double spin chain systems, such as NH_4CuCl_3, have also been studied using ESR and other techniques by Takatsu *et al* (1997) and Kurniawan *et al* (1999). However, it is worth remarking that the ladder character of $KCuCl_3$ is still under discussion. Cavadini *et al* (1999) believe that this material is better described as weakly coupled dimers. Hopefully this controversy will be solved in the near future.

The values of the exchange couplings that have been reported for $KCuCl_3$ locate the material in the strong rung coupling limit, as occurs for the $Cu_2(C_5H_{12}N_2)_2Cl_4$ compound, as explained earlier. For this reason it is natural for this author to suggest the use of (probably pulsed) high magnetic fields for the study of H_{c1}, which is the magnetic field at which the gapped spin state becomes gapless (for results with high fields see Shiramura *et al* (1997)). The aim would be to investigate whether the interesting physics reported by Chaboussant *et al* (1998b) is also present in $KCuCl_3$, especially regarding the possible presence of incommensurate spin correlations. Also, the chemical replacement of Cu ions by Zn or Ni ions would add to the ongoing discussion on the influence of vacancies on the physics of ladders and spin-Peierls systems, as discussed earlier in the paper (see Martins *et al* (1997) and references therein and also Sandvik *et al* (1997)).

4. Conclusions

In this review the experimental aspects of the study of ladder materials have been discussed, with emphasis on the relation with the high-T_c cuprates and contrasting the results with theoretical predictions. After a considerable effort, a variety of experiments have clearly confirmed the predicted existence of a spin gap in two-leg ladders, a feature that in the form of a pseudogap also appears in the underdoped two-dimensional cuprates. This is an important achievement of theoretical calculations, showing that, at least in spin systems and low dimensions, the models and many-body tools available are powerful enough to make reliable predictions. Even in the context of Zn-doped ladders a good agreement theory–experiment has been reported. Here small amounts of vacancies produce a considerable enhancement of the antiferromagnetic correlations in their vicinity and the ladders develop long-range order out of an apparently disordering procedure. Some other undoped ladders are in the strong rung coupling regime and the values of their couplings are such that they can be study in high magnetic fields, leading to a rich phase diagram that is also in good agreement with theoretical studies. Overall, the analysis of ladders in the absence of mobile holes seems under good control.

Once carriers are added to some of the available ladder compounds, a metal–insulator transition has been observed. At ambient pressure the carriers seem confined to move along

the ladders. As the pressure increases, the hole movement along the rung direction is enhanced and superconductivity appears in the [14–24–41] ladder. Pressure is presumed to increase the interladder couplings. Actually, it has become clear that such couplings are not negligible in several real ladders even in the undoped regime, causing transitions to antiferromagnetic states at low temperatures. While most authors agree with the notion that hole pairs are created on the ladders, probably by the mechanism predicted by the theorists, what triggers the transition to the superconducting phase is still under discussion. It may be that the interladder hopping is important to prevent the system from forming a CDW of pairs, which some experiments have detected at low-pressure. In this respect a large pressure is needed to provide extra mobility to the carriers, but too much pressure would conspire against the formation of pairs on the individual ladders. This may explain the existence of an optimal pressure. In addition, theoretical studies have shown that in the undoped regime an apparently small interladder coupling may destroy the spin gap and transform the ground state into a gapless antiferromagnet. Since the presence of spin gap features is important for the superconductivity predicted by the theorists, once again it is concluded that too much pressure may be detrimental for superconductivity.

Some experimental aspects are still controversial, notably the value of the spin gap as the hole concentration and pressure changes in [14–24–41]. Some NMR experiments associate the closing of the spin gap with the appearance of superconductivity. However, other NMR and neutron scattering experiments at slightly smaller pressures report a very robust spin gap. Hopefully these differences will be clarified in the near future. Resistivity measurements for this compound have found that the system becomes metallic both along the leg and rung directions at the optimal pressure. Similarities of this behaviour with results for two-dimensional cuprates have been here remarked by the author. A possible underdoped-like regime could exist in [14–24–41] in a narrow pressure window. Note that, regardless of the one-versus two-dimensional character of the superconductivity, x-ray experiments have confirmed the survival of the ladder substructures in the [14–24–41] material under high pressure. Thus, this compound is the *first* Cu oxide superconductor with a non-square-lattice arrangement. In addition, the resistivity versus temperature on the [14–24–41] ladder is linear at several concentrations adding to the list of features held in common with the two-dimensional cuprates. Several other similarities have been discussed in the paper. Certainly much can be learned from a superconducting compound that has the same Cu and O building blocks as the high-T_c materials.

The overall conclusion is that the analysis of ladder compounds has already developed into a fruitful area of research, and quite challenging and interesting results have become available in recent years. Among the most notable discoveries are a novel Cu oxide superconducting material with a ladder-dominated structure, and several other compounds with a clear spin gap in their spectrum. Further work in the context of ladders will probably keep on providing key information to unveil the mystery of the origin of superconductivity in the cuprates and the behaviour of electrons in transition metal oxides in general.

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