Classification
Physics Abstracts
74.70 — 71.55J

Superconductivity, localization and crystallographic phase transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$

W. Kang, G. Collin, M. Ribault, J. Friedel, D. Jérôme, J.M. Bassat⁺, J.P. Coutures⁺ and Ph. Odier⁺

Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France

⁺ CRPHT-CNRS, 45071 Orléans Cedex 2, France

(Reçu le 11 mai 1987)

Résumé.— Nous présentons une étude par résistivité de la supraconduction de la série $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ à l'aide d'échantillons caractérisés par analyse thermogravimétrique en ce qui concerne la teneur en oxygène. On observe la supraconductivité d'une part pour des valeurs de x non nulles avec un maximum de T_c au voisinage de la transition de phases tétragonal-orthorhombique et d'autre part dans le composé non-substitué $\text{La}_2\text{CuO}_{4-y}$. Une localisation importante des électrons est observée lorsque $x \approx 0,04$. Ces résultats sont en accord avec un modèle BCS simple pour lequel le remplissage de bande est déterminé par le dopage au strontium. L'existence de localisation pourrait provenir de la compétition entre les effets des lacunes d'oxygène et du dopage au strontium. Lorsque $x \approx 0,04$ la situation de bande demi-remplie permet les diffusions de type Umklapp. Nos résultats suggèrent une contribution des fluctuations antiferromagnétiques au mécanisme de "pairing" supraconducteur.

Abstract.— We report a resistive investigation of superconductivity in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ on samples which have been analysed by thermogravimetric techniques for oxygen deficiency determination. A maximum superconductive transition temperature is observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ near the tetragonal-orthorhombic phase transition, together with a resurgence of high temperature superconductivity in non-substituted $\text{La}_2\text{CuO}_{4-y}$. Drastic localization effects are observed in the vicinity of $x = 0.04$ with no sign of superconductivity at low temperature. These observations are coherent with a simple BCS scheme with a band filling dominated by Sr-doping and localization effects dominated by an interplay between O vacancies and Sr-doping. This situation leads to half-filling of the band near $x = 0.04$ with enhanced electron localization via Umklapp scattering through a near nested Fermi surface. Moreover, our data suggest some contribution of antiferromagnetic fluctuations to the superconducting pairing mechanism.

The recent report of superconductivity at a temperature higher than 30K in a ternary lanthanum-alkaline earth copper oxide by Bednorz and Muller [1] has stimulated a very impressive amount of work and has raised several fundamental experimental and theoretical problems which are a challenge for solid-state chemists and physicists.

The high T_c superconducting phases belong to a class of materials which have been around for quite some time: the lanthanum copper oxides La_2CuO_4 [2]. The structure of La_2CuO_4 studied in details by Longo and Raccach [3] shows it derives from the tetragonal structure of the 2D magnetic perovskite K_2NiF_4 but also exhibits a small orthorhombic distortion. Later, metallic conductivity was reported in the solid solution $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (M=alkaline earth) [4] and the group of Caen has studied in details the oxygen intercalation in this class of materials and shown they usually are oxygen deficient, namely

$\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$ [5]. In the present work we deal with materials which are either non-substituted or Sr substituted. There exists a consensus in the recent literature regarding the optimum amount of Sr substitution. It is around $x = 0.15$ where both T_c is the highest ($\approx 35\text{K}$) and the diamagnetic expulsion is the largest ($\approx 50\%$).

However, the La_2CuO_4 family exhibits a wealth of interesting features which are worth mentioning as they could be related to the occurrence of superconductivity.

(i) A small orthorhombic distortion exists in La_2CuO_4 at room temperature and vanishes at a temperature of 533K [3] above which the tetragonal K_2NiF_4 structure becomes stable.

(ii) Substitution of Sr for La preserves the distorted orthorhombic structure of lower temperature but increases the average valence charge of the

copper ions from the charge Cu^{2+} of La_2CuO_4 , in order to maintain charge neutrality.

(iii) Oxygen is known to deintercalate and reintercalate easily in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ ($y \geq 0$) even at moderate temperature and pressure, with a strong concomitant influence on transport properties [5].

Also, several experiments [6-9] on these materials have recently proved the dominant role played by the oxygen stoichiometry in the occurrence or disappearance of the superconductivity phenomena. Low oxygen content, i.e. high oxygen vacancy concentration, which promotes a decrease in the net hole concentration, favors carrier localization and possibly suppresses superconductivity phenomena. It has thus been considered as an important point to evaluate quantitatively the net oxygen content of several materials in which superconductivity properties have been studied.

Hence, the main purpose of this work is a study of the superconductivity occurrence in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ series in relation with Sr substitution, content of oxygen vacancies and the proximity of the tetragonal to orthorhombic ($T \rightarrow 0$) distortion.

Our results confirm that divalent alkaline-earth substitution is not a prerequisite for the observation of superconductivity in the La_2CuO_4 series [9]. Moreover, a detailed investigation at various substitution levels suggest the possibility of an interplay between the $T \rightarrow 0$ phase transition and superconductivity which is reminiscent of the interplay between superconductivity and charge density wave formation observed in 2D layered dichalcogenides [10].

All oxides studied in this work were prepared in the same way : mixing of freshly calcined lanthanum oxide, copper oxide and strontium carbonate with subsequent firing in air, followed by several grinding and annealing procedures. Final treatment consists in overnight annealing of pressed pellets at 1100°C in air and spontaneous cooling after switching off the furnace. X-ray powder patterns performed on Guinier-Laine camera (CuK_α) indicate that the materials are perfectly single-phased, no trace of impurity can be detected even on overexposed photographs. The materials exhibit at room temperature the orthorhombic distortion up to $x = 0.09$ and are strictly tetragonal for higher strontium concentrations. It is the same source of materials which has been used for an X-ray determination of the $T \rightarrow 0$ phase diagram [11].

Small parallelepipedic samples of typical size $\approx 0.5 \times 0.5 \times 6 \text{ mm}$ were cut in the sintered pellets with a diamond saw and used for resistivity measurements with four silver paint contacts. Either low frequency AC or DC currents were used to measure resistivity.

The oxygen content has been determined by the weight loss of the sample under reducing conditions.

A symmetrical micro-balance from SETARAM (1500) has been used between 20 and 1000°C . The sintered samples were ground in an agath mortar just before their introduction in the thermobalance. A typical weight of 100 to 200 mg has been used. The sample is then out gassed for an hour under vacuum (10^{-1} torr) at room temperature in order to remove part of the adsorbed species. Argon is then introduced at a flow rate of a few litres per hour. The temperature is then raised up to 1000°C at a rate of 300°C/h . An initial weight loss is observed between 20 and 550°C , followed by a range of temperatures in which no weight reduction is observed. At 1000°C the weight remains constant (under Ar) at least for more than an hour. After that initial step, Ar - 5% H_2 is introduced in the thermobalance at the same flow rate as previously. The sample is thus reduced rapidly, in 30min, in its constituents La_2O_3 , SrO and Cu metal. It was checked that the weight remains stable for more than one hour after complete reduction.

The resistivity data at various substitution levels below 60K are presented in figure 1. All samples for $0.08 \leq x \leq 0.20$ exhibit superconductivity. The critical temperature in figure 2a is defined by the temperature corresponding to the mid-point of the resistivity transition. The width ΔT of the superconducting transition is characterized by the temperature incre-

Fig.1.- Temperature dependence of the resistivity versus the Sr-substitution ratio. The inset shows the current-voltage characteristics of the $x = 0.15$ sample at 4.2 K .

ment between 10% and 90% of the resistive transition.

Furthermore, we may notice from figure 1 a drastic dependence of T_c and of the normal state resistivity on x . The value $x = 0.15$ provides about the lowest normal state resistivity which goes along with the optimum range for superconductivity. This was also derived from the concentration dependence of the Meissner effect [12] which shows the maximum fraction of ideal diamagnetism (about 50%) around $x \approx 0.15 - 0.20$. The inset of figure 1 shows the behaviour of the resistance at 4.2K versus DC current for $x = 0.15$. The low value of the critical current may be attributed to the granular character of the material but the critical current is still much larger at $x = 0.15$ than in the case of "pure" $\text{La}_2\text{CuO}_{4-y}$ which will be discussed later in this article.

Data of T_c and transition width versus x are reported in figure 2a. A maximum of T_c is clearly observed at $x = 0.15$. A minimum width at $x = 0.15$

Fig.2.- a) Critical temperatures and transition widths for various samples, $\square$ denotes the temperature of the anomaly for the $x = 0.06$ sample as explained in the text. b) Phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$.

is expected as T_c is passing through a maximum at the same value of x . However, figure 2a unambiguously shows that the drop of T_c observed on either sides of $x = 0.15$ is a genuine effect. It cannot be attributed to some kind of smearing of the transition. The $T_c = 6.6\text{K}(\square)$ point corresponds to a small but sharp drop of the resistivity occurring at this temperature in a $x = 0.06$ sample. However, this sample does not show zero resistivity below T_c . This anomaly is probably related to superconductivity but it is by no means a bulk phenomenon at $x = 0.06$. At the concentration $x = 0.04$ the temperature coefficient of the resistance is negative at low temperature with no sign of any superconducting anomaly down to 4.2K (Fig. 3).

Figure 2b deals with the interplay between the $T \rightarrow 0$ phase transition and superconductivity. The $x = 0.10$ and 0.12 data points have been taken from a recent X-ray study [11]. The dashed line is a guide

Fig.3.- Resistivity behaviour in $x = 0.02$ and $x = 0.04$ samples. Localization is evident at low temperature.

for the eye. Since the slope of the crystallographic phase transition line is likely to go to $-\infty$ as the transition temperature approaches zero temperature for thermodynamical reasons we feel confident that figure 2b is a fair representation of the phase diagram in the vicinity of $x = 0.15$. Moreover, the diagram of figure 2b is in fair agreement with neutron diffraction studies performed on powder samples [13] which imply that the $T \rightarrow 0$ transition of the $x = 0.15$ sample is located above 60K. It also indicates that the vanishing of the orthorhombic distortion represents the optimum situation for the onset of superconductivity.

The amount of additional holes (electrons) and relative weight losses determined from thermogravimetric studies are given in table I. We notice that the additional hole concentration is always smaller than the amount inferred from the Sr concentration but increases more or less monotonously with x . In the case of Sr-substituted La_2CuO_4 the oxygen vacancy concentration is in the range of a few percent. The hole concentration estimated by the charge neutrality is thus in the range of 3 to $9 \times 10^{20}\text{cm}^{-3}$ from $x = 0.08$ to $x = 0.15$. These measurements are in general agreement with previous results from Raveau *et al.* [14]. As far as pure La_2CuO_4 is concerned, the sample slowly cooled from 1000°C in air gives a small but significant vacancy concentration of about 4% excess electrons per formula unit. One has thus to account for oxygen vacancies which decrease the hole concentration. Two possibilities can be considered: Lanthanum vacancies coming from structural basis considerations [15] and/or negative charge carrier excess.

As shown in figure 2a, we confirm the existence of a superconducting transition in unsubstituted $\text{La}_2\text{CuO}_{4-y}$ which is usually reported as exhibiting a semiconducting behaviour at low temperature

[8,16]. In our sample, the onset of superconductivity in pure $\text{La}_2\text{CuO}_{4-y}$ is quite different from what it is in Sr-substituted materials. The resistivity of $\text{La}_2\text{CuO}_{4-y}$ is fairly high at room temperature and increases further by a factor about 50 down to the superconducting transition (Fig. 4). Given the sensitivity of our measuring system we can say that a zero resistance is achieved below T_c as long as the current passing through the sample does not exceed about $10\mu\text{A}$ (see insert of Fig.4). The critical current of 4.2K is roughly 10^3 times lower than that of the $x = 0.15$ samples.

Fig.4.- Temperature dependence of the resistivity of $\text{La}_2\text{CuO}_{4-y}$ under three different magnetic fields. The two insets show the current-voltage characteristics at 4.2K and the critical field temperature dependence.

Furthermore, the shift of the transition under magnetic field ($dH_c/dT \approx 1.12\text{T/K}$) displayed in figure 4 supports the superconducting nature of the resistive anomaly of "pure" $\text{La}_2\text{CuO}_{4-y}$. Considering the quite similar values of T_c and dH_c/dT values in pure and Sr-substituted $\text{La}_2\text{CuO}_{4-y}$, we may infer that the electronic structure should not be that different in both cases. However, superconductivity in the present $\text{La}_2\text{CuO}_{4-y}$ sample does not seem to be a bulk phenomenon. The critical current is extremely low and a preliminary attempt to measure the Meissner effect has failed to detect more than 0.1% flux expulsion [17]. Also in this sample, we observed a weak resistivity anomaly at around 230K which seems to correspond with that from susceptibility measurements [18,19].

Thermogravimetric results reported in table I do require some comments. The oxygen deficiency is small in all Sr-substituted samples in agreement with the early work of Michel and Raveau [5] and with a neutron diffraction study [16] establishing an upper limit of 1% for oxygen vacancies in

Table I.- Results from the thermogravimetry. — $\Delta m/m$ measured from 1 000 °C. The relative weight loss between 20 and 550 °C is smaller than 4×10^{-3} for the Sr-substituted sample.

x	$-\Delta m/m$	Estimated composition	Excess concentrations of electrons (−) or holes (+)
0.00A	3.86×10^{-2}	$\text{La}_2\text{CuO}_{3.98}$	− 0.04
0.00B	3.86×10^{-2}	$\text{La}_2\text{CuO}_{3.98}$	− 0.04
0.09	4.06×10^{-2}	$\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_{3.97}$	+ 0.03
0.10	4.155×10^{-2}	$\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_{3.99}$	+ 0.08
0.11	4.14×10^{-2}	$\text{La}_{1.89}\text{Sr}_{0.11}\text{CuO}_{3.98}$	+ 0.07
0.15	4.20×10^{-2}	$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{3.97}$	+ 0.09

$\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_{4-y}$. On the other hand, "pure" $\text{La}_2\text{CuO}_{4-y}$ exhibits a non zero content of oxygen vacancies which amounts to a concentration of 4% additional electrons in samples A and B. Sample A which shows superconductivity was slow cooled in air after firing at 1100°C whereas sample B quenched in air exhibits a more insulating character and no superconductivity at low temperature. Quite similarly Cava and van Dover [8] could not find superconductivity in a quenched powder of La_2CuO_4 .

Taken in isolation, the results reported here are not necessarily contradictory with the various theories of strong coupling superconductivity based on a non conducting pure and stoichiometric La_2CuO_4 compound and on superconductivity associated with doping [20-23]: in this light, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ would be superconductive because of Sr doping ; $\text{La}_2\text{CuO}_{4-y}$ because of O deficiency. However, two points must be stressed : (i) the behaviour of the conductivity above T_c , which is very sensitive to O deficiency, does not look like being due to the approach of a metal-insulator phase change by gap opening ; (ii) the rather small sensitivity of T_c on O deficiency [9]. They show that simple minded strong coupling scheme should be modified to take such observations into account.

One can also refer to the simple BCS scheme [24-26], treating Sr doping and O deficiency effects as only changing the band filling in a rigid band model. In such a picture, T_c should increase in the strongly doped tetragonal phase when $x - 2y$ is reduced, because the Fermi level E_F would approach the central van Hove anomaly E_0 (Fig. 5a). Below a critical value of $(x - 2y)$, the orthorhombic phase should become more stable, with the Fermi level near to but above the lower van Hove anomaly E_1 (Fig. 5b). Further reduction of $(x - 2y)$ would push the Fermi level away from E_1 and this could reduce T_c . Hence, a maximum of T_c could occur near the boundary of the phase change, as observed experimentally. Analogous interplays between

superconductivity and phase change are known : cubic to tetragonal phase change in quasi 1D V_3Si type of compounds with doping [27], suppression of a CDW under pressure in quasi 2D transition dichalcogenides such as 2H-NbSe_2 or $4\text{H}_b\text{-TaS}_2$ [10]. In all cases, the phase change is associated with a reduction in the density of states near the Fermi level, which lowers T_c . In the same rigid band model, the T_c observed in $\text{La}_2\text{CuO}_{4-y}$ could be attributed to a raising of the Fermi level near to the second van Hove anomaly E_2 (Fig. 5b).

Fig.5.- Band structure in the simple BCS scheme : a) Tetragonal phase, b) Orthorhombic phase.

We believe that such a simple minded description also requires some modifications.

Because the $T \rightarrow 0$ distortion is small (about 1%), the energy splitting of figure 5b is modest. As a result, for any position of the Fermi level between the two van Hove anomalies, they should add their effects, leading to a T_c not very sensitive to band filling in this range [28]. To explain the total absence of superconductivity in the vicinity of $x = 0.04$, one must invoke the presence, in this range of Sr concentration and in our samples (with $y \approx 0.02$), of some new insulating phase due to a nesting process. Indeed, because $x - 2y \approx 0$ in this range, the conduction band should be about half filled. In the simplest approximation for the copper $(x^2 - y^2)$ d band, where Cu-O-Cu transfers are treated as perturbations, exact nesting conditions for $Q = \pm \frac{\pi}{2a} \pm \frac{\pi}{2b}$ are realized in the orthorhombic [28] as well as in the tetragonal phase (Fig. 6a,b). For such nesting wave vectors commensurate with a reciprocal lattice vector, Umklapp terms in electron scattering could become relevant and promote the suppression of charge degrees of freedom with a concomitant

Fig.6.- Nesting conditions for half filled band : a) tetragonal phase ; b) orthorhombic phase.

vanishing of superconductivity. This situation is reminiscent of superconductive-insulator transition in organic superconductors of the $(\text{TMTTF})_2\text{X}$ series, where a spin density wave or spin Peierls state develop at low temperature even at moderate values of the interchain Coulomb repulsion when g_3 Umklapp terms become pertinent [29,30]. There is indeed some evidence of a SDW state below 240 K for small values of x in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ series [19,31]. More work is needed to check whether our samples with $x \approx 0.04 \pm 0.02$ show some evidence of such a phase change.

For $x = 0$, the practical absence of Meissner effect in our samples suggests a very inhomogeneous superconductivity, which probably only develops along the grain boundaries with an inhomogeneous repartition of O vacancies. If the grains are insulating, the preceding discussion suggests that they are nearly stoichiometric in O, and that O vacancies concentrate near the grain boundaries. Indeed the weak resistivity anomaly observed by us and others [18,19] at about 240K in our undoped samples suggests that the center of the grains has the expected SDW phase. The finding of the same O deficiency in A and B samples by thermogravimetric study, which is a volume determination of O vacancies, supports the picture for a surface only superconductivity of sample A.

If O vacancies are concentrated, in our undoped samples, near the grain boundaries, this means that the local shift of Fermi level due to O vacancies is larger in the superconductive phase than that due to the average value $y = 0.02$. One could thus be locally nearer to a van Hove anomaly of the orthorhombic phase. This would lead to a higher expected T_c . However a second effect might then have to be taken into account : if a sizeable fraction of the O vacancies are in the CuO_2 planes, each O vacancy and its neighbouring Cu^+ ions provide a strong scattering center for the conductive electrons, which could produce 2D localization effects on these electrons. This would explain the difference of $\rho(T)$ behaviour of our samples between $x = 0$ and $x = 0.08$.

Data on annealing superconducting samples under vacuum [32] are in fair agreement with our picture as an increase of O vacancies should shift the Fermi level towards the centre of the band, promote localization and suppress superconductivity.

In conclusion, the purpose of this note was to draw attention on two major experimental evidences (i) the role of oxygen vacancies on the superconductivity phenomenon of $\text{La}_2\text{CuO}_{4-y}$ or lightly Sr substituted samples ($x < 0.08$) and (ii) the role of Sr substitution on both the $T \rightarrow 0$ transition and the occurrence of a maximum in the superconducting T_c .

The observations are coherent with a simple BCS

scheme and a band filling governed by a balance between O vacancies and Sr substitution. Transport properties data suggest that disorder induced localization plays a crucial role on the behaviour of the resistivity above the onset of superconductivity in $\text{La}_2\text{CuO}_{3.98}$. We also propose that the band becomes half-filled at a very low concentration of Sr-substitution ($x \approx 0.04$) leading to a carrier localization *via* Umklapp scattering in near nested 2D bands with no loss in the spin degrees of freedom some what similar to the observation in 2:1 organic conductors. More experiments on varying and controlling the content of O vacancies, especially in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ with x small or equal to zero, are under progress to check the validity of such a model [33].

Finally, a realistic model should analyse in some details the coupling term leading to the e-e pairing (thus the weak phonon mode associated with the $T \rightarrow 0$ transition near x_c could be partly responsible for the maximum of T_c observed at x_c) [26].

But the failure to observe any isotope effect on oxygen [34] could suggest e-e coupling through exchange of antiferromagnetic fluctuations [35]. A wealth of experimental and theoretical evidences support the existence of such spin-fluctuation mediated interchain pairing in quasi-1D organic superconductors up to temperatures of about 30-40K [36,37].

This work has been partly supported by the DRET contract 86/057. We thank J.C. Ameline and T. Pourthie for their skillful technical help.

References

- [1] BEDNORZ J.G. and MULLER K.A., *Z. Phys.* **B64** (1986) 189.
- [2] FOEX M., MANCHERON A. and LINE L. C. R. *Heb. Acad. Sci. Paris* **250** (1960) 3027.
- [3] LONGO J. and RACCAH P.M., *J. Solid State Chem.* **6** (1963) 526.
- [4] SHAPLYGIN I.S. KAKHAN B.G. and LAZAREV V.B., *Zh. Neorg. Khim.* **24** (1979) 1478 [*J. Inorg. Chem.* **24** (1979) 820].
- [5] MICHEL C. and RAVEAU B., *Rev. Chim. Miner.* **21** (1984) 407.
- [6] SHAMOTO S., HOSOYA S., ONODA M. and SATO M., submitted to *Japan J. Appl. Phys.*
- [7] TAKAGI H., UCHIDA S., KITAZAWA K. and TANAKA S., preprint.
- [8] CAVA R.J., van DOVER R.B., BATLOGG B. and RIETMAN E.A., *Phys. Rev. Lett.* **58** (1987) 408.
- [9] BEILLE J., CABANEL R., CHAILLOUT C., CHEVALLIER B., DEMAZEAU G., DESLANDES F., ETOURNEAU J., LEJAY P., MICHEL C., PROVOST J., RAVEAU A., SULPICE A., THOLENCE J.L. and TOURNIER R., *C.R. Heb. Acad. Sci. Paris*, under press.
- [10] FRIEND R.H., JÉROME D., FRINDT R.F., GRANT A.J. and YOFFE A.D., *J. Phys.* **C10** (1977) 1013.
- [11] MORET R., POUGET J.P. and COLLIN G., submitted to *Europhys. Lett.*
- [12] van DOVER R.B., CAVA R.J., BATLOGG B. and RIETMAN E.A., *Phys. Rev.* **B35** (1987) 5337.
- [13] CAVA R.J., SANTORO A., JOHNSON D.W., Jr. and RHODES W.W., preprint.
- [14] NGUYEN N., CHOISNET J., HERVIEU M. and RAVEAU B., *Solid State Chem.* **39** (1981) 120.
- [15] LEBLANC, CHOISNET J., BASSAT J.M. and ODIER Ph., to be published.
- [16] JORGENSEN J.D., SCHUTTLE H.-B., HINKS D.G., CAPONE Jr. D.W., ZHANG K., BRODSKY M.B. and SCALAPINO D.J., *Phys. Rev. Lett.* **58** (1987) 1024.
- [17] SENOSSI S. and MONOD P., private communication.
- [18] JANOSSY A., private communication to FRIEDEL J.
- [19] GREENE R.L., MALETTA H., PLASKETT T.S., BEDNORZ J.G. and MULLER K.A., submitted to *Solid State Commun.*
- [20] BASKARAN G., ZON Z. and ANDERSON P.W., *Solid State Commun.*, under press.
- [21] ALEXANDROV A.S., RANNINGER J. and ROBASKIEWICZ S., *Phys. Rev.* **B33** (1986) 4526.
- [22] PRELOBSEK P., RICE T.M. and ZHANG F.C., preprint.
- [23] CYROT M., submitted to *Solid State Commun.*
- [24] SCHUTTLE H.D., JORGENSEN J.D., HINKS D.C., CAPONE Jr. D.W. and SCALAPINO D.J., preprint.
- [25] LABBE J. and BOK J. *Europhys. Lett.* **3** (1987) 1225.
- [26] BARISIĆ S., BATISTIĆ I. and FRIEDEL J. *Europhys. Lett.* **3** (1987) 1231.
- [27] LABBE J., *Phys. Rev.* **172** (1968) 451.
- [28] FRIEDEL J., to be published.
- [29] COULON C., DELHAES P., FLANDROIS S., LAGNIER R., BONJOUR E. and FABRE J.M., *J. Physique* **43** (1982) 1059.
- [30] EMERY V.J., BRUINSMA R. and BARISIĆ S., *Phys. Rev. Lett.* **48** (1982) 1039.
- [31] BEDNORZ J.G., TAKASHIGE M. and MÜLLER K.A., *Europhys. Lett.* **3** (1987) 379.
- [32] SHAMOTO S., HOSOYA S., ONADA M. and SATO M., *Jpn. J. Appl. Phys.* **26** (1987) 493.
- [33] KANG W. *et al.*, to be published.
- [34] Communication of AT&T at MRS, Conference April, 1987.
- [35] EMERY V.J., *Synthetic Metals* **13** (1986) 21.
- [36] BOURBONNAIS C. and CARON L.G., *Phys. Rev. Lett.* (1987) to be published.
- [37] JÉROME D., CREUZET F. and BOURBONNAIS C., *Proceedings of the Yamada Conference XV*, p. 329, Lake Kawaguchi, Yamanashi, Japan, May 26-30, 1986.