

## Interpretation of doping phenomena in high- $T_c$ superconductors

LEENA CHANDRAN and LAURENS JANSEN

Physics Department, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

**Abstract.** On the basis of an indirect-exchange pairing mechanism of superconductivity we present a consistent interpretation of doping phenomena in both hole-doped as well as electron-doped high- $T_c$  superconductors. We argue that in all these materials the unifying feature is the existence of a correlated narrow band of electron states formed due to doping. Numerous experimental evidences for the occurrence of such a band (reflectivity, thermoelectric power, electrical resistivity, X-ray absorption, point-contact tunneling etc.) now exist.

Assuming the existence of such a band it was earlier shown that the indirect-exchange (superexchange) coupling between electrons in this band via closed-shell oxygen anions is attractive in the s-wave channel and leads to high- $T_c$  superconductivity. Within the framework of this pairing mechanism, recent doping experiments (for both types of doping) can be given a unified interpretation. In addition, definitive predictions of the doping conditions under which critical temperatures are expected to enhance, are made.

**Keywords.** Doping phenomena; indirect-exchange phenomena.

### 1. Introduction

As a basis for our interpretation of doping phenomena in high- $T_c$  superconductors we argue that in all these materials (hole-doped as well as electron-doped), the unifying feature is the existence of a correlated narrow band of electron states formed at the Fermi surface as a result of doping. Based on recent work (Jansen 1988; Jansen and Block 1989) in which an indirect-exchange mechanism for pairing of electrons in these states *via closed-shell oxygen anions* was outlined, we analyse and interpret consistently the effect of various chemical substitutions on the superconductivity in these compounds (Jansen and Chandran 1990).

The existence of a narrow band of states near the Fermi surface was first postulated by Tsidilkovski and Tsidilkovski (1988) in a phenomenological model aimed at explaining the temperature dependence of electrical resistivity and thermoelectric power for ceramics Y–Ba–Cu–O and La–Sr–Cu–O. On the side of theory, such a band was assumed to exist (Jansen and Block 1988), while extending an earlier theory of superconductivity in simple metals (in terms of exchange between conduction electrons via the metal-cation cores) (Schmidt *et al* 1982) to the high- $T_c$  superconductors.

Unambiguous experimental evidence was provided by Takahashi *et al* (1988, 1989) from angle-resolved photoemission experiments on  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$ . In addition, these results showed that the states at the Fermi surface have (predominantly) O 2p character, with little Cu 3d admixture. In conjunction with inverse photoemission data on the same compound by Drube *et al* (1989), exhibiting a resonance near the O 2s core-level threshold analogous to that observed for the occupied states at the Fermi level (Takahashi *et al* 1988), this was strong evidence for the band-like (Fermi-liquid) states. A critical appraisal of the information provided by these spectroscopic methods has been given, very recently, by Sawatzky (1989).

Numerous experiments on different high- $T_c$  superconductors have confirmed the above findings (Jansen and Block 1989). In particular, we mention that Minami *et al* (1989) attribute the narrow band-crossing the Fermi level in  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$  to states of "heavy electrons" formed by strong correlation effects. Because of the latter feature, such bands are not reproduced in conventional band-structure calculations. Suzuki (1989) investigated the Hall coefficients and optical properties of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  thin films, finding an anomalous absorption band near the top of the valence band, which develops with doping. Sarma *et al* (1989), from XAS experiments on  $\text{YBa}_2\text{Cu}_{2.7}\text{Fe}_{0.3}\text{O}_{6.9}$ , find that the observed 528.1 eV absorption peak cannot be attributed to stoichiometry-induced oxygen valence-shell holes at the Fermi level. Instead, this feature must be due to new states created by doping.

Similar characteristics pertain to the non-cuprate superconductors  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  and  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ . Matsuyama *et al* (1989), from an ultraviolet photoemission study of  $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$ , find a clear Fermi edge structure which they interpret in terms of new electronic states created by doping. Hegde *et al* (1989), from X-ray photoelectron spectra of  $(\text{Ba}, \text{K})\text{BiO}_3$ , observe a shift in the O 1s absorption peak to lower binding energy in going from  $\text{Ba}_{0.8}\text{K}_{0.2}\text{BiO}_3$  (non-superconducting) to  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  (superconducting,  $T_c = 30$  K). In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  they find the energy shift to be somewhat larger ( $T_c = 93$  K). Barring a relaxation source for the shift, this phenomenon must be interpreted as due to extra "oxygen" states formed upon doping. Accordingly, the largest shift is found in Y-Ba-Cu-O with the highest  $T_c$ . On the theoretical side, Matsumoto *et al* (1989) have proposed a mechanism for the spontaneous formation of a narrow band at the Fermi level upon doping, starting from a  $d$ - $p$  mixing model. The new band is situated in the charge-transfer gap of the undoped cuprates and has O  $2p$  character. The authors reason that such a band may lower the free energy of the system through a many-electron effect. They quote results reported by D Shindo and Y Fukuda (private communication), that narrow-band states at the Fermi level do *not* occur in non-superconducting Bi and Tl compounds (Ca in part replaced by Y), from which they conclude that electrons in the narrow band are Cooper-pair partners in high- $T_c$  superconductivity. Fujimori *et al* (1989) recently made a careful analysis of the states at the Fermi level in the superconductors  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  and  $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\delta}$ , as well as in the insulator  $\text{Bi}_4\text{Sr}_3(\text{Ca}_{0.58}\text{Y}_{0.42})_3\text{Cu}_4\text{O}_{16+\delta}$  from photoemission spectra. They conclude that the extra ("split-off") oxygen states *also exist* in the insulator, although the whole spectrum is shifted to higher binding energy, suppressing their density of states at the Fermi level. As for the Y-Ba-Cu-O and La-Sr-Cu-O superconductors, these authors conclude that the split-off states are *induced* by excess oxygen and substituted strontium, respectively.

The concept of extra electron states also applies to "electron-doped" superconductors of which the first,  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ , with a maximum  $T_c$  in the mid-20 K range for  $x = 0.15$ , was discovered by Tokura *et al* (1989). Soon after, it was found that Pr, Sm, Eu and Th instead of cerium give similar results, and that oxygen can in part be replaced by fluorine. Since the oxidation state of the Ce-ion is (close to) + 4, negative charges must counterbalance the Ce doping. Accurate X-ray absorption spectra measured by Tranquada *et al* (1989) showed that initially the system reacts by forming  $\text{Cu}^{1+}$ . However, these materials are *not* superconducting. It is only after "reducing" in argon or nitrogen, resulting in removal of a small amount of oxygen (order of 1%), that the system becomes superconducting. A simple explanation is that doping by itself only leads to the formation (building up) of a

narrow conduction band of oxygen 2p character and that electrons, liberated upon reduction, populate this band, and are responsible for the observed superconductivity.

## 2. Indirect exchange mechanism for superconductivity

In an earlier paper, Schmidt *et al* (1982), developed a model for superconductivity based on an assumed relationship between superconductivity and the phenomenon of superexchange (indirect exchange) in magnetic insulators such as NiO. In the latter material, unpaired electrons on two Ni cations are coupled via a closed-shell oxygen ( $O^{2-}$ ) anion. In extrapolating this well-known effect to metals, it was demonstrated that under stringent conditions also conduction electrons, in a tight-binding description, may couple via the closed shells of metal cations (e.g.  $Cs^{1+}$  in metallic Cs), with the interaction being attractive in the *s*-wave channel. Adopting a BCS approach, a one-to-one correspondence was found between model predictions and experiment, regarding occurrence or absence of superconductivity, for 21 simple metals. Of the alkali metals, only Cs is predicted to become superconducting, under pressure, in agreement with experiment.

The same mechanism of superexchange pairing is applicable to high- $T_c$  superconductors (Jansen 1988; Jansen and Block 1989). Here, conduction electrons are coupled via oxygen-anion ( $O^{2-}$ ) closed shells, in direct analogy with superexchange in insulating oxides. The charge distributions of the anions are taken to be Wannier functions approximated by a simple Gaussian function with parameter  $\alpha$ . The conduction electrons on the other hand are described, within a tight-binding approximation, by a (Gaussian) parameter  $\beta$  in theta (Bloch) functions (Boon *et al* 1977, 1978) localized at the sites of the oxygen anions. The Cooper pairing mechanism is assumed to be isotropic with anions, in principle arbitrarily placed, distributed uniformly in the crystal. The superconducting transition temperature, in analogy with the BCS form, is given by ( $W < 0$ )

$$T_c = \langle A\omega \rangle \exp(-1/|W|). \quad (1)$$

Here  $|W|$  is the superexchange coupling strength, proportional to the density of states and a sensitive function of the parameters  $\alpha$  and  $\beta$ . The pre-exponential factor  $\langle A\omega \rangle$  is a temperature characteristic of the type of coupling. For computational convenience, a body-centered cubic (bcc) and a hexagonal close-packed (hcp) arrangement of the oxygen anions were chosen, for which the results were found to be practically identical. The value of  $\alpha$  for the oxygen ( $O^{2-}$ ) anion was taken from earlier calculations on superexchange in non-conducting oxides. The parameter  $\beta$  is correlated with the oxygen density in the crystal. For small  $\beta$  (low oxygen density), it is found that  $|W|$  increases steeply with  $\beta$ , reaches a plateau, and then decreases rapidly for larger  $\beta$  (higher oxygen density). Numerical results for  $W$  were obtained (Jansen and Block 1989) for the high- $T_c$  families (nominal compositions)  $Tl_2(Bi_2)Ca_{N-1}Ba_2(Sr_2)Cu_NO_{2N+4}$  and  $Tl_1Ca_{N-1}Ba_2Cu_NO_{2N+3}$ , with varying number  $N$  of  $CuO_2$  layers per molecular unit. Adopting one gauge value of  $|W|$ , for  $Tl_2(N = 1)$ , the agreement with experimental results for the transition temperatures was found to be quantitative. It should be noted that to yield superconductivity in the 100 K range the conduction electrons must be relatively "heavy" ( $m^*/m_e \approx 5$ ). The theory predicts a maximum in  $T_c$  for  $N = 3$  in the  $Tl_2$ -family, and for  $N = 3$  or 4 in the  $Tl_1$ -series (depending upon the precise oxygen

stoichiometry), in striking agreement with experiment. For these and all further details of the calculations we must refer to Jansen and Block (1989). We emphasize that on the basis of the model, superconductivity in metals, i.e. low- $T_c$ , and in high- $T_c$  oxides differs only in the values for the parameters  $\beta$  (conduction electrons) and  $\alpha$  (closed-shell cations or oxygen anions), as well as in different effective-mass ratios  $m^*/m_e$ . Phonons are not explicitly considered, although they may play an indirect role (time dependence of closed-shell anion positions).

### 3. Application to doping phenomena

The question arises whether the superexchange model is also capable of accounting for the principal phenomena observed in high- $T_c$  superconductors under different doping conditions (varying dopants, and dopant concentrations). We consider the compound  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with maximum  $T_c \approx 36$  K at  $x \approx 0.15$ . Resistivity measurements by Ellman and co-workers (1989) showed that all samples with  $x > 0.02$  are metallic at high temperatures and that superconductivity sets in at  $x = 0.055$ . Precisely at this dopant concentration the room-temperature resistivity drops, by a factor of 23. In terms of the model, the extra band of conduction states, being formed for  $x < 0.055$ , is populated at that concentration. As the density of states increases with  $x$ , the critical temperature rises steeply since  $T_c$  depends exponentially on  $W$ . The pre-exponential factor in (1), being a temperature characteristic of the type of coupling, is  $x$ -independent. Upon further doping the system becomes more metallic (the Fermi vector  $|k_F|$  increases). As a result, overlap between the conduction-electron, tight-binding, wavefunction and that of the oxygen  $2p$  valence shell decreases sharply. Consequently, the superexchange coupling rapidly vanishes, resulting in a steep drop in  $T_c$ . This effect has been observed by Torrance *et al* (1988): a saturation of  $T_c$  occurs at  $\approx 36$  K from  $x \approx 0.15$  to  $0.24$  after which it begins to decrease. Beyond  $x \approx 0.32$  superconductivity has disappeared, although the metallic conductivity still increases.

We next turn to the corresponding ( $N = 1$ ) members of the  $\text{Tl}_2$ -,  $\text{Bi}_2$ - and the  $\text{Tl}_1$ -families, i.e. (nominally)  $\text{Tl}_2(\text{Bi}_2)\text{Ba}_2(\text{Sr}_2)\text{CuO}_6$  and  $\text{Tl}_1\text{Ba}_2\text{CuO}_5$ . Superconductivity in these compounds depends sensitively on the method of preparation, sintering temperatures, etc. Least problematic is  $\text{Tl}_2$  ( $N = 1$ ), which by careful experimentation is found to exhibit a sharp transition at 83 K (Parise *et al* 1989). For  $\text{Bi}_2$  ( $N = 1$ ), Ramakrishnan and Rao (1989) reported transient superconductivity at  $60 \pm 20$  K in some of the samples. The compound  $\text{Tl}_1$  ( $N = 1$ ) was found not to be a superconductor until Ku *et al* (1989) recently established a (metastable)  $T_c$  around 10 K. These features are accurately reproduced in the superexchange model. Starting from the gauge value of  $|W|$  for  $\text{Tl}_2$  ( $N = 1$ ), the values for  $\text{Bi}_2$  ( $N = 1$ ) and  $\text{Tl}_1$  ( $N = 1$ ) are calculated (comparing unit-cell dimensions) to be considerably lower, lowest for  $\text{Tl}_1$  ( $N = 1$ ), on the steep part of the  $W(\beta)$  curve (Jansen and Block 1989). This also implies that small changes in stoichiometry will have a large effect on  $T_c$  for the latter two compounds (Jansen and Block 1989).

Of importance for elucidating the superconductivity mechanism are experiments of *additional* (isovalent or non-isovalent) doping of high- $T_c$  superconductors, first carried out on Bi–Ca–Sr–Cu–O systems. Soon after the discovery by Maeda *et al* (1988), of a superconducting phase with  $T_c > 105$  K, it became known that this system

has (at least) two different phases: one with  $T_c$  near 110 K (high- $T_c$  phase), of nominal composition  $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$  and one with  $T_c$  near 85 K (low- $T_c$  phase), nominally  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ . Somewhat later, several groups (Chavira *et al* 1988; Ganapathi *et al* 1988; He *et al* 1988; Sunshine *et al* 1988; Takano *et al* 1988) independently established that the high- $T_c$  phase was stabilized, and its yield increased by adding Pb to the reactants. Present refined techniques render the synthesis of a practically pure 110 K phase possible. It now appears likely that Pb addition affects predominantly only the rate and the equilibrium composition of the solid-state reaction. The addition has little effect on the density of states at the Fermi surface and thus on the superconducting transition temperature (usually, a small  $T_c$  enhancement of order 10 K is reported). For details, we refer to careful analyses by Chavira *et al* (1988) and He *et al* (1988).

Supplementary doping has also been carried out on the compound  $\text{YBa}_2\text{Cu}_3\text{O}_6$  (non-superconducting) (Carron *et al* 1989) and on  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 80$  K) (Miyatake *et al* 1989) with calcium replacing in part yttrium. For the first compound  $T_c$  increases from 0 K to 50 K (optimally  $x = 0.2$  in  $\text{Y}_{1-x}\text{Ca}_x$  doping) whereas in the second system, an increase in  $T_c$  from 80 K to 90 K is found for an optimal  $x = 0.1$ . The first case reflects the onset of superconductivity where the  $T_c(x)$  curves is very steep, whereas for the second compound  $T_c(x)$  is near its maximum. This is in close analogy with the situation in Sr-doped  $\text{La}_2\text{CuO}_4$ .

Among the dopants in high- $T_c$  superconductors, those which imply "electron doping" (this can be accomplished e.g. by replacing  $(2+)$  Ca, Sr or Ba ions with  $(3+)$  cations such as Y, La etc.) are of crucial importance as regards the pairing mechanism. A striking effect on  $T_c$  was recently found by Ku *et al* (1989), substituting in part La for Ba in  $\text{Tl}_1$  ( $N = 1$ ). They find that the mid-point  $T_c$  increases from 10 K ( $x = 0$ ) to a (sharp) value of 42 K for  $x = 0.2$ , in single-phase  $\text{Tl}_1\text{Ba}_{2-x}\text{La}_x\text{CuO}_5$ . The same authors also obtained  $T_c$  enhancement in  $\text{Bi}_2$  ( $N = 1$ ), from  $< 6$  K for  $x = 0$  to (mid-point) 27 K for  $x = 0.5$ , with zero resistivity at 19 K, in  $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_6$ . These results provide additional evidence that electron pairs are the charge carriers in the superconductors. Several groups (see Fukushima *et al* 1989 for references) have now established that in the system  $\text{Bi}_2\text{Ca}_{1-x}\text{Y}_x\text{Sr}_2\text{Cu}_2\text{O}_{8+\delta}$ ,  $T_c$  shows an initial increase in the region of small  $x$  followed by a lowering at larger  $x$ . Similar results were obtained by Den and Akimitsu (1989) on Sr-to-La doping in  $\text{Bi}_2$  ( $N = 2$ ), by Koyama *et al* (1989) on Ca-to-Nd, Pr doping, also in  $\text{Bi}_2$  ( $N = 2$ ), and by Somasundaram *et al* (1989) on Ca-to-Ln doping (Ln = Y or rare earth) in  $\text{Tl}_{0.8}$  ( $N = 2$ ) and  $\text{Tl}_1$  ( $N = 2$ , Sr<sub>2</sub> for Ba<sub>2</sub>). Bauhofer *et al* (1989) also examined Sr-to-La doping in the  $\text{Bi}_2$ -compound, arriving at the conclusion that the extra positive charge is overcompensated in that the crystal accommodates one extra oxygen anion for each  $(+3)$  La cation. However, Groen *et al* (1989) find no trace of such an overcompensation, which was probably due to the use of an inaccurate oxygen analysis method by Bauhofer *et al* (1989).

All these  $T_c(x)$  curves are strikingly of the same form as that of the hole-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , implying one and the same physical origin. Thus, both hole doping (indirectly) and electron doping (directly) can lead to an increase of conduction-electron density, enhancing the density of states at the Fermi level. At the same time this enhancement decreases the overlap between conduction-electron and oxygen valence-shell wavefunctions and therefore lowers the indirect-exchange coupling. The result is an initial increase in  $T_c$  with  $x$ , followed by a broad maximum and then a rapid  $T_c$  lowering. In some cases a steep increase in  $T_c$  at small doping is due to a

phase change, as found with Y-doping Tl–Sr–Cu–O (Inoue *et al* 1989). For small doping the composition is  $\text{Tl}_1(\text{Sr}_{2-z}\text{Y}_z)\text{CuO}_y$ , with quite low  $T_c$  ( $< 30$  K). Upon increasing  $z$  beyond 0.3, the phase  $\text{Tl}_1(\text{Sr}_{1-z}\text{Y}_z)\text{Sr}_2\text{Cu}_2\text{O}_y$  takes over, similar to  $\text{Tl}_1\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_7$  ( $T_c$  of about 80 K). Thus, the appearance of the second phase causes steep rise in  $T_c$ . For  $z > 0.35$  the transition temperature decreases, apparently for the same reason as in (La, Sr)–Cu–O.

A particularly interesting case of non-isovalent additional doping is provided by the system  $(\text{Y}_{1-x-y}\text{Ca}_y)\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_z$ , recently investigated in detail by Neumeier *et al* (1989) with  $z = 6.95 \pm 0.02$ . If we assume that the oxidation state of Pr is larger than +3, then we have to do with double non-isovalent substitutions, one with (+2) Ca and one with ( $> +3$ ) Pr. However, this question is not settled in the literature (for detailed references see Inoue *et al* 1989, also Koyama *et al* 1989). The effect of substituting Pr for Y in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is of great interest, since Pr is the only lanthanide which has a pronounced (decreasing) effect on  $T_c$ . The close correspondence of  $T_c$  vs Pr concentration to theoretical predictions based on the Abrikosov–Gor'kov theory has been interpreted as evidence for magnetic pair-breaking effects. On the other hand, the substitution of ( $> +3$ ) Pr for (+3) Y implies electron doping, and it may be expected that the experiments will show both aspects of the doping process. The (+2) Ca serves in part to “monitor” the Pr pair breaking. Assuming a double role for the Pr substitution, Neumeier *et al* (1989) obtain from their data a Pr valence of  $3.95 \pm 0.20$  and a clear indication of pair breaking. On the other hand, Nahm *et al* (1989) ascribe the decrease in  $T_c$  as a function of Pr concentration entirely to a “hole-filling” effect in a BCS type equation for  $T_c$ , thus ignoring possible pair-breaking, and obtain good agreement with experiment. Clearly, more experimental information is needed on this system (e.g. the possibility of (+1) Cu formation, in analogy with the situation in (+4) Ce-doped  $\text{Nd}_2\text{CuO}_4$  (Tranquada *et al* 1989) before a detailed theoretical analysis is feasible.

We emphasize that  $T_c$  enhancement can be expected only for small dopant fractions. In addition, the oxygen content must not increase, since this by itself neutralises excess positive dopant charge. Post-treatment in nitrogen or argon, as with (Nd, Ce)–Cu–O, should be applied. As a third aspect, replacement of Bi or Tl with a higher-charged cation such as (5+) Sb, is not an effective means of  $T_c$  enhancement unless it substitutes for Sr or Ca. In the Tl–O and Bi–O layers, such doping is easily balanced by changes in stoichiometry, pre-empting the increase in  $T_c$ . The reported high  $T_c > 132$  K by Liu *et al* (1989) in (Pb-stabilized)  $\text{Bi}_{2-x}\text{Sb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$  is, consequently, quite puzzling; these results have not been substantiated by other groups (Sastry *et al* 1989; Dabrowski *et al* 1989; Dou *et al* 1989). However, quite recently Chandrachud *et al* (1989) also established a sharp transition to zero resistance at 132 K in (lead-free)  $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ . As mentioned earlier, if Sb could substitute for Sr or Ca, then the large increase in  $T_c$  would not be surprising. On the other hand, small doping by La or Y, substituting for Ca or Ba in  $\text{Tl}_2$  ( $N = 3$ ), followed by post-treatment in nitrogen or argon, may well lead to a  $T_c$  higher than 125 K, the present record.

## References

- Bauhofer W, Mattausch HJ, Kremer R K, Murugaraj P and Simon A 1989 *Phys. Rev.* **B39** 7244  
 Boon M H, Mueller F M and Myron H W 1977 *Solid State Commun.* **21** 911

- Boon M H, Mueller F M and Myron H W 1978 *Phys. Rev.* **B18** 3810
- Chandrachood M R, Mulla I S and Sinha A P B 1988 *Appl. Phys. Lett.* **55** 1472
- Chavira E, Escudero R, Rios-Jara D and Leon L M 1988 *Phys. Rev.* **B38** 9272
- Dabrowski B, Richards D R, Hinks D G, Hannon R H, Peng W, Lee H, Genis A P, Melim V J and Kimball C W 1989 *Physica* **C160** 281
- Den T and Akimitsu J 1989 *Jpn. J. Appl. Phys.* **28** L193
- Dou S X, Liu H K, Tan N X, Sheng Y J and Jones W K 1989 *Physica* **C158** 97
- Drube W, Himpfel F J, Chandrashekar G V and Shafer M W 1989 *Phys. Rev.* **B39** 7328
- Ellman B, Jaeger H M, Katz D P, Rosenbaum T S, Cooper A S and Espinosa G P 1989 *Phys. Rev.* **B39** 9012
- Fujimori A, Tokura Y, Eisaki H, Takagi H, Uchida S and Sato M 1989 *Phys. Rev.* **B40** 7303
- Fukushima N, Niu H, Nakamura S, Takeno S, Hayashi M and Ando K 1989 *Physica* **C159** 777 and references therein
- Ganapathi L, Krishna S, Murthy K, Vijayaraghavan R and Rao C N R 1988 *Solid State Commun.* **67** 967
- Groen W A, de Leeuw D M and Stollman G M 1989 *Solid State Commun.* **72** 697
- He Q, Yu D, Chang S, Wang R and Zhang H 1988 *Phys. Lett.* **A133** 441
- Hegde M S, Barboux P, Chang C C, Tarascon J M and Venkatesan T 1989 *Phys. Rev.* **B39** 4752
- Inoue O, Adachi S and Kawashima S 1989 *Jpn. J. Appl. Phys.* **28** L1375
- Jansen L 1988 *Physica* **C156** 501
- Jansen L and Block R 1988 *Physica* **C152** 1
- Jansen L and Block R 1989 *Physica* **A161** 385
- Jansen L and Chandran L 1990 (submitted to *J. Phys. C*).
- Koyama K, Kanno S and Noguchi S 1989 *Jpn. J. Appl. Phys.* **28** 1354
- Ku H C, Tai M F, Shi J B, Shieh M J, Hsu S W, Hwang G H, Ling D C, Watson-Yang T J and Ling T Y 1989 *Jpn. J. Appl. Phys.* **28** L923
- Liu H, Liezhao C, Ling Z, Zhiqiang M, Xiaoxian L, Bai X, Xianglei M, Guien Z, Yaozhong R, Zhaojia C and Yuhang Z 1989 *Solid State Commun.* **69** 867
- Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Jpn. J. Appl. Phys.* **27** L209
- Matsumoto H, Sasaki M and Tachiki M 1989 *Solid State Commun.* **71** 829
- Matsuyama H, Takahashi T, Katayama-Yoshida H and Okabe Y 1989 *Phys. Rev.* **B40** 2658
- McCarron III E M, Crawford M K and Parise J B 1989 *Solid State Chem.* **78** 192
- Minami F, Kimura T and Takekawa S 1989 *Phys. Rev.* **B39** 4788
- Miyatake T, Gotoh S, Koshizuka N and Tanaka S 1989 *Nature (London)* **341** 41
- Nahm K, Cha Bo Young and Kim Chul Koo 1989 *Solid State Commun.* **72** 559
- Neumeier J J, Bjornholm T, Maple M B and Schuller I K 1989 *Phys. Rev. Lett.* **63** 2516
- Parise J B, Torardi C C, Subramanian M A, Gopalakrishnan J and Sleight A W 1989 *Physica* **C159** 239
- Ramakrishnan T V and Rao C N R 1989 *J. Phys. Chem.* **93** 4414
- Sarma D D, Sen P, Carbone C, Cimino R and Gudat W 1989 *Phys. Rev.* **B39** 12387
- Sastry P V P S S, Yakhmi J V and Iyer R M 1989 *Solid State Commun.* **71** 935
- Sawatzky G A 1989 *Nature (London)* **342** 481
- Schmidt W W, Block R and Jansen L 1982 *Phys. Rev.* **B26** 3656
- Somasundaram P, Vijayaraghavan R, Nagarajan R, Seshadri Ram, Umarji A M and Rao C N R 1989 *Appl. Phys. Lett.* (to be published)
- Sunshine S A *et al* 1988 *Phys. Rev.* **B38** 893
- Suzuki M 1989 *Phys. Rev.* **B39** 2312
- Takahashi T, Matsuyama H, Katayama-Yoshida H, Okabe Y, Hosoya S, Seki K, Fujimoto H, Sato M and Inokuchi H 1988 *Nature (London)* **334** 691
- Takahashi T *et al* 1989 *Phys. Rev.* **B39** 6636
- Takano M, Takada J, Oda K, Kitagouchi H, Miura Y, Ikeda Y, Tomii Y and Mazaki H 1988 *Jpn. J. Appl. Phys.* **27** L1041
- Tokura Y, Takagi H and Uchida S 1989 *Nature (London)* **337** 345
- Torrance J B, Tokura Y, Nazzari A I, Bezing A, Huang T C and Parkin S S P 1988 *Phys. Rev. Lett.* **61** 1127
- Tranquada J M, Heald S M, Moodenbaugh A R, Liang G and Croft M 1989 *Nature (London)* **337** 720
- Tsidilkovski I M and Tsidilkovski V I 1988 *Solid State Commun.* **66** 51