JOURNAL OF SOLID STATE CHEMISTRY **124,** 199–204 (1996)
ARTICLE NO. 0226

Transport and Magnetic Properties of $La_2NiO_{4+\delta}$ ($0 \leq \delta \leq 0.25$)

A. Demourgues, P. Dordor, J.-P. Doumerc, J.-C. Grenier,[1] E. Marquestaut, M. Pouchard, A. Villesuzanne, and A. Wattiaux

Institut de Chimie de la Matière Condensée de Bordeaux, C.N.R.S., Château Brivazac, Av. du Dr. Schweitzer, 33608 Pessac, France

Received September 26, 1994; in revised form January 22, 1996; accepted January 29, 1996

Materials with $La_2NiO_{4+\delta}$ composition, δ ranging between 0 and 0.25, have been prepared either by solid state reaction or electrochemical oxidation; their electrical conductivity, thermoelectric power, and magnetic susceptibility behaviors are reported. The compounds remain semiconducting in the whole range of composition and, at low temperature, the resistivity increases with δ. The sign of the Seebeck coefficient changes for $\delta \approx 0.2$ and the thermal variation shows complex behavior. $La_2NiO_{4.03}$ exhibits a thermally activated hopping and an antiferromagnetic ordering. When δ increases, variable range hopping or nearest neighbor hopping, involving at least two types of carriers, can account for the transport properties. The magnetic behavior of materials with $\delta \leq 0.18$ reveals either 3D or 2D magnetic correlations whereas the susceptibility of $La_2NiO_{4.25}$ ($La_8Ni_4O_{17}$) follows a Curie–Weiss law below 170 K; a change in the electronic configuration of the nickel ions arises beyond this temperature. © 1996 Academic Press, Inc.

INTRODUCTION

Structural, transport, and magnetic properties of K_2NiF_4-type oxides have been investigated for many years and a renewed interest has been found for these studies since the discovery of superconductivity of the "model compound" La_2CuO_4.

It is well known that, according to the conditions of preparation, La_2CuO_4 and La_2NiO_4 crystallize with an oxygen excess (δ) that strongly influences their properties. Complex phase diagrams of $La_2CuO_{4+\delta}$ and $La_2NiO_{4+\delta}$ have been reported as a function of δ (1–5).

The stoichiometric compounds show semiconducting behavior but the oxygen excess causes a hole doping which results for $La_2CuO_{4+\delta}$ in an insulator to metal transition ($\delta \approx 0.05$) and superconducting behavior at low temperature ($T < T_C \approx 44$ K) whereas $La_2NiO_{4+\delta}$ remains semiconducting at low temperature as δ increases. At about 600 K, a smooth change from a semiconducting to a metallic-like behavior is observed for $La_2NiO_{4+\delta}$ but various interpretations disagree on its nature (6–8). The thermal dependence of the conductivity of $La_2NiO_{4+\delta}$ ($0 \leq \delta \leq 0.05$) has been described by Arrhenius laws with activation energies in the range 50–100 meV or in terms of Mott variable range hopping (6, 9–13).

The magnetic behavior of extra-oxygen doped $La_2NiO_{4+\delta}$ materials exhibits many similarities with that of the high T_C superconductors $La_2CuO_{4+\delta}$. Both compounds remain antiferromagnetically ordered above room temperature when nearly stoichiometric; this magnetic ordering disappears for $La_2CuO_{4+\delta}$ for $\delta \geq 0.02$ (1, 14) whereas for $La_2NiO_{4+\delta}$ it has been observed for δ values up to ≈0.15 (5). The magnetic susceptibility as well as the Néel temperature of $La_2NiO_{4+\delta}$ strongly depend on the δ value (5, 15–19) and highly stoichiometric La_2NiO_4 shows nearly temperature independent behavior above 80 K (15).

In previous works we have reported the intercalation of oxygen into oxide lattices using electrochemical oxidation in alkaline solution, at room temperature (20–22). For instance, thanks to this new method of "Chimie Douce," the range of the δ values was extended up to $\delta = 0.12$ and 0.25 for $La_2CuO_{4+\delta}$ and $La_2NiO_{4+\delta}$, respectively. Transport properties and superconducting behavior of $La_2CuO_{4+\delta}$-related materials have been described in detail elsewhere (1, 23).

In this work our attention is focused on $La_2NiO_{4+\delta}$ materials ($0 \leq \delta \leq 0.25$). A preliminary TEM study of the electrochemically prepared materials with $0.17 \leq \delta \leq 0.25$ revealed their complex structure and the presence of commensurate and/or incommensurate superstructures which were assigned to the ordering of interstitial oxygen atoms (24). Several superstructure lattices have been identified leading us to conclude that these materials contain various line-phase microdomains with $\delta = 1/4, 1/6, 1/8, \ldots$ compositions (25). Special attention was paid to the compound $La_2NiO_{4.25}$ whose structure was refined on the basis of a TEM study and of neutron diffraction powder data at 300 and 9 K (26, 27). It was shown that the additional oxygen atoms order both in tetrahedral sites within the La_2O_2 layers and along the $[111]_T$ direction of the basic K_2NiF_4-type tetragonal structure, which results in a monoclinic

---

[1] To whom correspondence should be addressed.

0022-4596/96 $18.00
Copyright © 1996 by Academic Press, Inc.
All rights of reproduction in any form reserved.

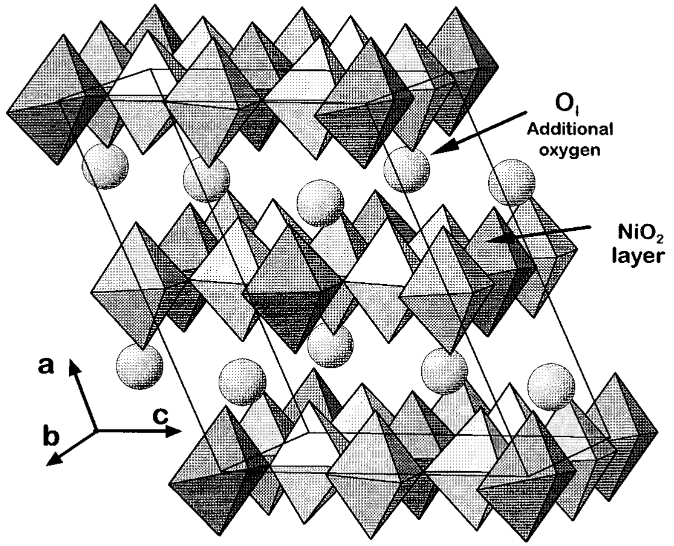

FIG. 1. Representation of the monoclinic structure of $La_2NiO_{4.25}$ ($La_8Ni_4O_{17}$) showing the NiO_2 layers and the tetrahedral coordination of interstitial oxygen atoms.

supercell (C_2 space group), the new definite compound being formulated $La_8Ni_4O_{17}$. Its structure is represented in Fig. 1.

In this paper we report the electrical and magnetic properties of $La_2NiO_{4+\delta}$ materials as a function of δ ($0.03 \leq \delta$ 0.25). These data, especially those concerning $La_8Ni_4O_{17}$ ($\delta = 0.25$), will be used for discussing a band diagram that will be published in a forthcoming article.

EXPERIMENTAL

The samples were prepared using two methods:

—Solid state reaction. A stoichiometric mixture of NiO and La_2O_3 is dissolved in nitric acid, and then, after evaporation, the mixture of nitrates is slowly heated up to 700°C. The samples were pelleted (8 mm ϕ, 2 mm thickness, $\approx$0.4 g mass) and finally annealed for 48 h, at 1200°C, in air, which leads to a material with $La_2NiO_{4.14}$ composition. $La_2NiO_{4.03}$ was prepared by reducing the previous material under flowing argon ($p_{O_2} \approx 10^{-3}$ atm).

—Electrochemical oxidation of the starting materials. The electrochemical procedure has been previously described in detail (22). Experiments were carried out in alkaline solution (1 *N* KOH), at room temperature, in air, at constant potential (600 mV/HgO/Hg reference electrode). After electrochemical oxidation, the pellets were washed in distilled water under ultrasonics and then in ethanol, and were finally dried. The oxygen content was determined from the chemical analysis of trivalent nickel (iodometry or Mohr salt method). The $\delta = 0.11$ composition was obtained after polarizing $La_2NiO_{4.03}$ for 2 days and the $\delta = 0.18$ and 0.25 compositions after polarizing $La_2NiO_{4.14}$ for 3 and 5 days, respectively.

Electrical measurements were carried out with a conventional four probe method on ceramics. The sample density was close to 95% of the theoretical value for $\delta = 0.03, 0.11$, and 0.14 and close to 85% for $\delta = 0.18$ and 0.25. The thermal dependence of the magnetic susceptibility was measured in the range 4.2–300 K with a pendulum-type automatic susceptometer (Manics, DSM8 model) under a magnetic field of 1.8 T.

RESULTS

a. Electrical Conductivity Measurements

The thermal variation of the electrical conductivity of $La_2NiO_{4+\delta}$ ($50 \leq T \leq 300$ K) is given in Fig. 2. It shows semiconducting behavior in the whole composition range, the resistivity increasing with δ, at least below 120 K. The temperature dependence of the Seebeck coefficient (Fig. 3) reveals complex behavior and a change in the sign of α for the $0.14 < \delta < 0.18$ range (from p-type to n-type with increasing δ). This completely differs from what was observed for $La_2CuO_{4+\delta}$ whose electrical resistivity continuously decreases with increasing δ and which exhibits a p-

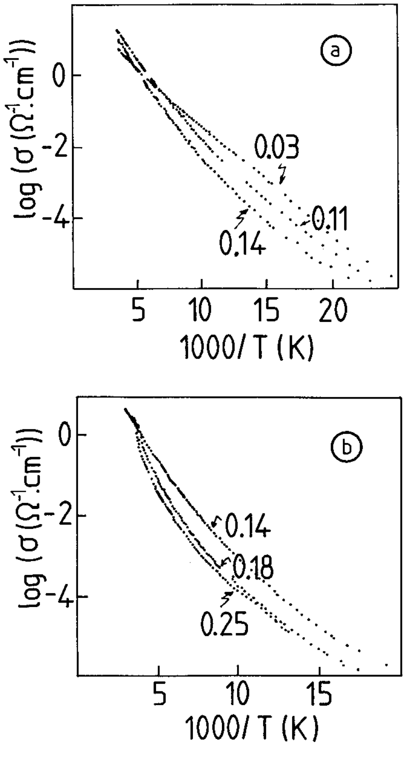

FIG. 2. Logarithm of the electrical conductivity vs inverse temperature for $La_2NiO_{4+\delta}$. (a) $\delta = 0.03$, 0.11, and 0.14. (b) $\delta = 0.14$, 0.18, and 0.25.

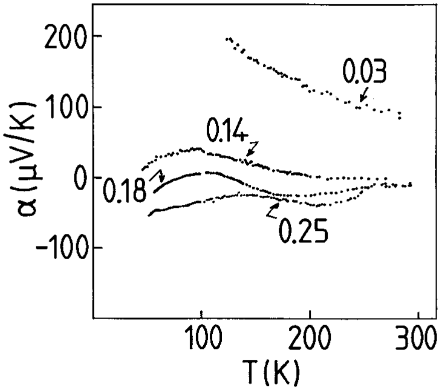

FIG. 3. Thermoelectric power vs temperature for $La_2NiO_{4+\delta}$ (δ = 0.03, 0.14, 0.18, and 0.25).

type metallic and bulk superconducting character for $\delta \geq 0.06$ (1).

In the present system, the results can be interpreted as follows.

The $\delta = 0.03$ composition obviously exhibits very different behavior from the other ones and will be examined first. The Seebeck coefficient of $La_2NiO_{4.03}$ can be expressed by

$$\alpha(T) = (k/e)(E_\alpha/kT + A), \quad [1]$$

where $A = 2$ and $E_\alpha = 0.02$ eV. Such behavior could account for a weak trapping of holes in the vicinity of intercalated oxygen defects. However, the activation energy for the conductivity ($E_\sigma = 0.065$ eV), which follows an Arrhenius law,

$$\sigma(T) = \sigma_0 \exp(-E_\sigma/kT), \quad [2]$$

is much larger than E_α. This denotes an activated carrier mobility ($E_\mu = E_\sigma - E_\alpha = 0.045$ eV) and suggests that the valence band states, originating from Ni 3*d* states, are localized and that charge transport involves a hopping process.

For $\delta = 0.25$, as previously reported (26), the neutron diffraction refinement of the crystal structure of $La_8Ni_4O_{17}$ ($La_2NiO_{4.25}$) revealed the existence of six different sites for nickel atoms (Fig. 4). At 9 K two of them are occupied by monovalent nickel (Ni(1) and Ni(4)), two by trivalent nickel (Ni(2) and Ni(3)), and two by nickel in a mixed valent state $Ni^{2+,3+}$ (Ni(5) and Ni(6)) : this charge disproportionation results from the ordering of the interstitial oxygen atoms within the La_2O_2 layers and the formation of … $-Ni^+-O_3^{5-}-Ni^+-$ … chains along the $[111]_T$ direction resulting from oxygen–metal electron charge transfer (26). This surprising presence of monovalent Ni^+ was claimed on the basis of previous ESR spectroscopy evidence (22). Then it is reasonable to assume that charge transport occurs by hopping between the nonlinked sites occupied by mixed valent nickel atoms as the temperature dependence of the thermoelectric power does not clearly reveal any thermally activated creation of carriers.

The decrease of the absolute value of the—negative—thermoelectric power as the temperature increases in the range $50 < T < 140$ K can be attributed to an increase of the electron concentration in the mixed valent nickel atoms. Actually the structure determined at room temperature showed that electrons are transferred from Ni(1) to Ni(5) and Ni(6) sites (27). As it will be shown in the band structure calculations (28), important structural distortions can give rise to a splitting of the valence band into a manifold of narrow bands, some of them overlapping at the Fermi level. This electronic structure being very sensitive to atomic displacements, a rearrangement of the bands is expected to occur as temperature changes, leading to the observed complex thermal dependence of the Seebeck coefficient.

The occurrence of a superstructure for $La_2NiO_{4.25}$ correlated with a charge density modulation in the NiO_2 layers also well accounts for the increase of the resistivity with δ, at least at low temperature: the concentration of nickel atoms involved in the hopping process decreases and hence the hopping probability becomes smaller as the number of available nearest neighbors with similar energy becomes smaller.

The dependence of the thermoelectric power on temperature as well as on δ can be explained if one assumes two types of carriers play a role in the transport process. Actually, at least for $\delta = 0.25$, our calculated band diagrams clearly predict the occurrence of two types of carriers,

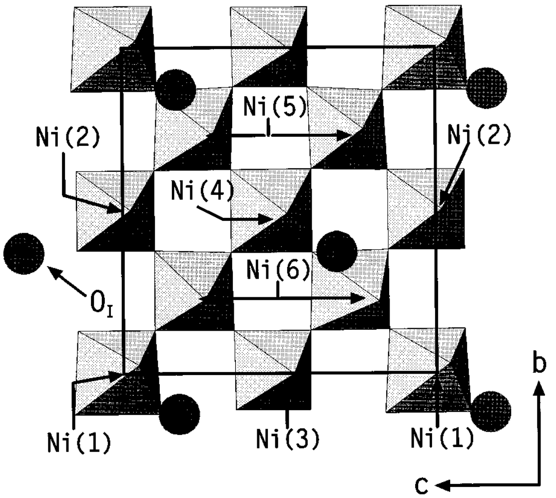

FIG. 4. NiO_2 layer showing the six different types of nickel cations resulting from the occurrence of a 2D charge modulation in $La_8Ni_4O_{17}$ ($La_2NiO_{4.25}$).

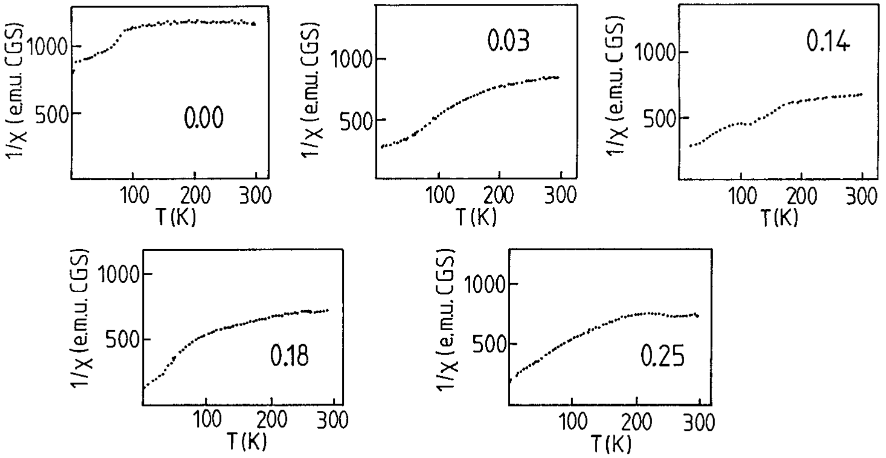

FIG. 5. Inverse magnetic susceptibility vs temperature for $La_2NiO_{4+\delta}$ ($\delta = 0$, 0.03, 0.14, 0.18, and 0.25).

which qualitatively accounts for the change in the sign of α either with temperature (e.g. for $\delta = 0.18$) or with composition (from negative for $\delta = 0.25$ to positive—in the whole temperature range—for $\delta = 0.14$). However, a more quantitative discussion of the variation of the sign of α with δ would obviously require a determination of the crystal structure and of the charge distribution for materials with $\delta < 0.25$.

Two mechanisms could account for the nonlinear variation of log (σ) as a function of the reciprocal temperature observed for most of the samples with $\delta > 0.03$. The first results from the above mentioned change in the band overlap with temperature, which could lead carriers with various thermal dependencies of mobility to contribute to the conductivity process.

On the other hand, the temperature dependence of the conductivity can be described by a Mott-type law (29):

$$\sigma(T) = \sigma_0 \exp(-B/T^n). \qquad [3]$$

Such a thermal variation suggests, as a second possible explanation, that variable range hopping becomes the predominant transport mechanism at low temperature. An electron jumping from a given site onto a site more distant than the nearest neighbors is possible provided that site energies of available sites are spread around E_F. This condition can be fulfilled if random potential fluctuations occur. Such fluctuations are often observed in mixed valent oxides where polaron formation may sometimes be frozen into local site distortions. For $\delta = 0.11$ the value of the exponent n in Eq. [3] was found to be close to 1/3. The earliest theory of variable range hopping—i.e. neglecting electron–electron interactions— predicts such a value of n for 2D systems (30) (instead of $n = 1/4$ for 3D systems), which would well agree with the crystal structure of the materials discussed here.

b. Magnetic Properties

The thermal variations of the inverse of the magnetic susceptibility for various compositions of the $La_2NiO_{4+\delta}$ system are reported in Fig. 5. The magnetic correlations appear very sensitive to the additional oxygen content (δ).

$La_2NiO_{4.00}$ exhibits a 3D antiferromagnetic ordering at $T_N = 330$ K and a weak ferromagnetic component appears below $T_{WF} = 80$ K. Similar behavior is observed for $La_2NiO_{4.03}$ with $T_{WF} = 65$ K and magnetization curves as a function of magnetic field show a weak ferromagnetic component of about 0.04 μ_B at 4.2 K. Such a weak ferromagnetism has also been observed in single crystals of $La_2NiO_{4+\delta}$ ($\delta = 0.05$ and 0.10) and attributed to spin canting (31).

For materials with $\delta \geq 0.14$, this weak ferromagnetism disappears at least down to liquid helium, which would mean that the 3D antiferromagnetic order vanishes. As previously suggested by various authors (2, 17, 18) this behavior is assigned to the occurrence of holes in the NiO_2 planes that would create ferromagnetic superexchange interactions competing with the usual Ni^{2+}–O^{2-}–Ni^{2+} antiferromagnetic ones. The resulting frustration destroys the 3D long range antiferromagnetic ordering (2). However, a hump is clearly seen in the thermal magnetic behavior of the compound with $\delta = 0.14$ (Fig. 5), which seems to corroborate recent studies of Yamada *et al.* (32) and Tranquada *et al.* (33) who observed below $T \approx 110$ K an incommensurate magnetic ordering for $\delta \approx 0.125$. For $\delta = 0.18$, such a hump is still observed but at much lower temperature ($T \approx 35$ K) and similar behavior is expected with regards to the complex microstructure of this compound (24).

However, the situation seems to be quite different for $La_2NiO_{4.25}$: EPR measurements (22) as well as neutron diffraction data (26, 27) of this definite compound

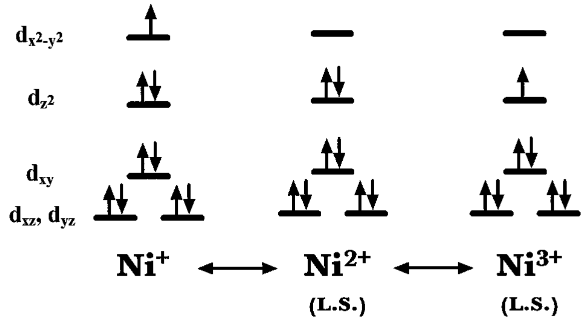

FIG. 6. Schematized representation of the disproportionation of Ni^{2+} cations leading to the various electronic configurations of the nickel cations in $La_8Ni_4O_{17}$.

($La_8Ni_4O_{17}$) did not reveal any magnetic ordering and the magnetic susceptibility measurements did not give any evidence of weak ferromagnetic component, which suggests that the compound remains paramagnetic over the whole range of temperature. In such a way, we assume for $T <$ 170 K a Curie–Weiss law of the form $\chi = \chi_0 + C_M/(T - \theta_P)$, with χ_0 (T.I.P.) $= 100 \times 10^{-6}$ emu/mol(Ni), $\theta_P \approx -80$ K, and $C_M \approx 0.33$ emu · K/mol(Ni).

As previously quoted, we evidenced by the structure refinement of this compound that the various electronic configurations of the six nickel cations are more or less close or intermediate between Ni^+, low spin Ni^{2+}, and low spin Ni^{3+} (as represented in Fig. 6) and that an electron transfer from interstitial oxygen to nickel occurs. The formulation of this compound can be then written $La_{16}(Ni^+)_2(Ni^{3+})_2(Ni^{2.5+})_4(O^{2-})_{32}(O_i^-)_2$. The mixed valent $Ni^{2.5+}$ ions in Ni(5) and Ni(6) sites can be considered as a mixture of an equal amount of Ni^{2+} and Ni^{3+}. Thus one can assume that two Ni^+ and four Ni^{3+} cations ($S = 1/2$) give a contribution of ≈0.28 emu · K/mol(Ni) to the Curie constant. The difference with the experimental value can be assigned either to some contribution of O_i^- anions ($S = 1/2$) or/and to the presence of some Ni^{2+} cations in a high spin state. This last assumption would result in a partial filling of the $d^*_{x^2-y^2}$ band, which is in agreement with the negative value of the Seebeck coefficient.

Then, beyond $T \approx 200$ K, the magnetic susceptibility remains almost steady with the temperature, which may be caused by a gradual change in the electronic configuration of Ni^{2+} cations from low spin ($S = 0$; $d_{z^2}^2 d_{x^2-y^2}^0$) to high spin ($S = 1$; $d_{z^2}^1 d_{x^2-y^2}^1$) state. Such a spin equilibrium is correlated with relaxing effects for the structure as we previously discussed (26, 27).

CONCLUSION

The electrochemical oxidation has allowed us to insert additional oxygen into La_2NiO_4 up to a δ value of 0.25. Electrical conductivity measurements show that these materials remain semiconducting over the whole composition range as it was previously reported for the solid solution $La_{2-x}Sr_x$ NiO_4 ($0 \le x \le 0.50$) (34). In addition no trace of superconductivity was detected. The complexity of the thermal variation of the thermoelectric power can be correlated to the fact that E_F lies in different overlapping σ^* narrow bands, leading to two types of carriers, which is confirmed by band structure calculations (28). Magnetic measurements show magnetic correlations up to $\delta \approx 0.18$, whereas $La_2NiO_{4.25}$ is paramagnetic over the whole range of temperature.

ACKNOWLEDGMENTS

The authors acknowledge J.-M. Bassat, J.-P. Loup, and P. Odier (C.R.P.H.T., CNRS Orléans) for fruitful discussions.

REFERENCES

1. J.-C. Grenier, N. Lagueyte, A. Wattiaux, J.-P. Doumerc, P. Dordor, J. Etourneau, and M. Pouchard, *Physica C* **202,** 209 (1992), and references therein.
2. J. Rodriguez-Carvajal, M. T. Fernandez-Diaz, and J. L. Martinez, *J. Phys.: Condens. Matter.* **3,** 3215 (1991).
3. D. E. Rice and D. J. Buttrey, *J. Solid State Chem.* **105,** 197 (1993).
4. H. Tamura, A. Hayashi, and Y. Ueda, *Physica C* **216,** 83 (1993).
5. K. Yamada, T. Omata, K. Nakajima, Y. Endoh, and S. Hosoya, *Physica C* **221,** 355 (1994).
6. P. Ganguly and C. N. R. Rao, *Mater. Res. Bull.* **8,** 405 (1973).
7. F. Gervais, P. Odier, and Y. Nigara, *Solid State Commun.* **56,** 371 (1985).
8. J.-M. Bassat, P. Odier, and J.-P. Loup, *J. Solid State Chem.* **110,** 124 (1994).
9. C. N. R. Rao, D. J. Buttrey, N. Otsuka, P. Ganguly, H. R. Harrison, C. J. Sandberg, and J. M. Honig, *J. Solid State Chem.* **51,** 266 (1984).
10. K. K. Singh, P. Ganguly, and J. B. Goodenough, *J. Solid State Chem.* **52,** 254 (1984).
11. M. Sayer and P. Odier, *J. Solid State Chem.* **67,** 26 (1987).
12. J.-M. Bassat, F. Gervais, P. Odier, and J.-P. Loup, *Mater. Sci. Eng. B* **3,** 507 (1989).
13. X. Granados, J. Fontcuberta, M. Vallet-Regi, M. J. Sayagues, and J. M. Gonzalez-Calbet, *J. Solid State Chem.* **102,** 455 (1993).
14. D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, *Phys. Rev. B* **36,** 4007 (1987).
15. D. J. Buttrey, J. M. Honig, and C. N. R. Rao, *J. Solid State Chem.* **64,** 287 (1986).
16. G. Aeppli and D. J. Buttrey, *Phys. Rev. Lett.* **61,** 203 (1988).
17. T. Freltoft, D. J. Buttrey, G. Aeppli, D. Vaknin, and G. Shirane, *Phys. Rev. B* **44,** 5046 (1991).
18. S. Hosoya, T. Omata, K. Nakajima, K. Yamada, and Y. Endoh, *Physica C* **202,** 188 (1992).
19. J. M. Tranquada, D. J. Buttrey, and D. E. Rice, *Phys. Rev. Lett.* **70,** 445 (1993).
20. A. Wattiaux, L. Fournès, A. Demourgues, N. Bernaben, J. C. Grenier, and M. Pouchard, *Solid State Commun.* **77,** 489 (1991).
21. J.-C. Grenier, A. Wattiaux, N. Lagueyte, E. Park, E. Marquestaut, J. Etourneau, and M. Pouchard, *Physica C* **173,** 139 (1991).
22. A. Demourgues, A. Wattiaux, J.-C. Grenier, M. Pouchard, J. Soubeyroux, J.-M. Dance, and P. Hagenmuller, *J. Solid State Chem.* **105,** 458 (1993).

23. J. C. Grenier, F. Arrouy, J-P. Locquet, C. Monroux, M. Pouchard, A. Villesuzanne, and A. Wattiaux, *in* ''Phase Separation in Cuprates'' (K. A. Muller and G. Benedeck, Eds.) p. 237. World Scientific, Singapore, 1994.
24. A. Demourgues, F. Weill, J.-C. Grenier, A. Wattiaux, and M. Pouchard, *Physica C* **192,** 425 (1992).
25. Z. Hiroi, T. Obata, M. Takano, Y. Bando, Y. Takeda, and O. Yamamoto, *Phys. Rev. B* **41,** 11665 (1990).
26. A. Demourgues, F. Weill, B. Darriet, A. Wattiaux, J.-C. Grenier, P. Gravereau, and M. Pouchard, *J. Solid State Chem.* **106,** 317 (1993).
27. A. Demourgues, F. Weill, B. Darriet, A. Wattiaux, J.-C. Grenier, P. Gravereau, and M. Pouchard, *J. Solid State Chem.* **106,** 330 (1993).
28. A. Villesuzanne, A. Demourgues, J-C. Grenier, J-P. Doumerc, A. Wattiaux, and M. Pouchard, to be published.
29. N. Mott, ''Metal-Insulator Transitions,'' 2nd ed., pp. 50–55. Taylor & Francis, London, 1990.
30. N. Mott, M. Pepper, S. Pollit, R. H. Wallis, and C. J. Adkins, *Proc. R. Soc. London A* **345,** 169 (1975).
31. K. Yamada, T. Omata, K. Nakajima, S. Hosoya, T. Sumida, and Y. Endoh, *Physica C* **191,** 15 (1992).
32. K. Yamada, T. Omata, K. Nakajima, Y. Endoh, and S. Hosoya, *Physica C* **221,** 355 (1994).
33. J. M. Tranquada, D. J. Buttrey, V. Sachan, and J. E. Lorenzo, *Phys. Rev. Lett.* **73,** 1003 (1994).
34. R. J. Cava, B. Batlogg, T. T. Palstra, J. J Krajewski, W. F. Peck, A. P. Ramirez, and L. W. Rupp, *Phys. Rev. B* **43,** 1229 (1991).