

## Superconductivity in layered nickel oxides

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**Abstract.** Likely presence of superconductivity in layered nickelates of  $K_2NiF_4$  structure is pointed out.

**Keywords.** Superconductivity; nickel oxides; lanthanum-strontium-nickel oxides.

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Since the discovery of superconductivity in  $La_{2-x}Ba_xCuO_4$  by Bednorz and Müller (1986) just over two years ago, there have been innumerable reports on high-temperature cuprate superconductors (Rao 1988a, b, c, d; Rao and Raveau 1989). The maximum  $T_c$  today is close to 130 K. All these cuprates have two-dimensional CuO sheets just as in  $La_{2-x}Ba_xCuO_x$ .  $La_{2-x}M_xCuO_4$  ( $M = Sr$  or  $Ba$ ) is tetragonal at room temperature and becomes orthorhombic at low temperatures, well before the superconducting transition. These oxides are marginally metallic at room temperature and have a nominal mixed valence of Cu. We have been interested in the study of  $La_2CuO_4$  and other transition metal oxides of  $K_2NiF_4$  structure for some years (Ganguly and Rao 1984; Rao and Ganguly 1987). Thus, we have compared the properties of transition metal oxides of  $K_2NiF_4$  structure especially those of the formula  $La_{2-x}Sr_xMO_4$  ( $M =$  transition metal) with the corresponding three-dimensional perovskite oxides (Rao *et al* 1988).

Among these layered oxides, of special interest is  $La_2NiO_{4+\delta}$  which is on the borderline between a metal and an insulator. The oxide shows a metal-insulator transition around 600 K in the *ab*-plane (Ganguly and Rao 1973; Rao *et al* 1984). The nickelate generally has an oxygen excess and the magnetic susceptibility is a strong function of  $\delta$ . For  $\delta = +0.001$ ,  $\chi(T)$  is temperature-independent below 300 K and for 0.05 there is a small cusp in  $\chi(T)$  at 160 K (Buttrey *et al* 1986). The presence of long-range quasi two-dimensional antiferromagnetic order below 200 K was suggested earlier. It is noteworthy that  $La_2CuO_4$  has an antiferromagnetic Néel temperature around 290 K (Mitsuda *et al* 1987) and shows an orthorhombic-tetragonal transition around 505 K.

$La_2CuO_4$  is suggested to be in a quantum-fluid state wherein the spins are ordered over long distances, but no measurable time-averaged moment is detectable (Shirane *et al* 1987). Recent neutron scattering studies (Aeppli and Buttrey 1988) show that in

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$\text{La}_2\text{NiO}_{4+\delta}$  also there is a strong influence of the orthorhombic-tetragonal transition ( $\sim 240\text{ K}$ ) on the magnetic correlations in the paramagnetic state. Furthermore, the in-plane magnetic dynamics as well as the three-dimensional Néel temperature depend strongly on oxygen stoichiometry. It is clear that  $\text{La}_2\text{NiO}_{4+\delta}$  is very similar to  $\text{La}_2\text{CuO}_{4+\delta}$  in most respects, the latter also showing a strong dependence of three-dimensional  $T_N$  on  $\delta$ . Above  $T_N$ , there are two-dimensional magnetic correlations in both the oxides. Oxygen-excess  $\text{La}_2\text{CuO}_{4+\delta}$  ( $\delta > 0.0$ ), however, shows superconductivity (Beille *et al* 1987; Jorgensen *et al* 1988), but  $\text{La}_2\text{NiO}_{4+\delta}$  does not.

$\text{La}_2\text{NiO}_{4+\delta}$  has two-dimensional NiO sheets and there is evidence for the presence of oxygen-holes in this oxide just as in the cuprate superconductors (Rao *et al* 1987, Rao 1988b; Chakraverty *et al* 1988). Recent studies in this laboratory show that metallic  $\text{LaNiO}_3$  also has a high proportion of oxygen holes. It seems therefore likely that a two-dimensional nickel oxide consisting of a fair proportion of nominal  $\text{Ni}^{3+}$  (or oxygen holes) should show superconductivity at reasonably high temperatures.

Leaving  $\text{La}_2\text{NiO}_{4+\delta}$ , the likely candidate for high  $T_c$  superconductivity would be oxides of the  $\text{Ln}_{2-x}\text{M}_x\text{NiO}_{4+\delta}$  where  $\text{Ln} = \text{La, Pr or Nd}$  and  $\text{M} = \text{Ca, Sr or Ba}$ . Here Ni is nominally mixed-valent. Unlike  $\text{LaNiO}_3$ ,  $\text{LaSrNiO}_4$  is an insulator (Mohan Ram *et al* 1986). Increasing the number of perovskite layers in the  $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$  or  $(\text{LaO})(\text{LaNiO}_3)_n$  series of which  $\text{La}_2\text{NiO}_4$  is the  $n = 1$  member, does not help since it only makes the material metallic similar to  $\text{LaNiO}_3$ . A system such as  $\text{La}_2\text{SrNi}_2\text{O}_{7+\delta}$  and  $\text{La}_3\text{SrNi}_3\text{O}_{10+\delta}$  is another possibility. Small amount of Cu doping ( $< 10\%$ ) in these layered nickelates would also favour superconductivity.

Preliminary measurements in this laboratory on the layered nickelates have shown indications of superconductivity in the Ln-Sr-Ni-O system. Although magnetic measurements are dominated by antiferromagnetic interactions due to  $\text{Ni}^{2+}$ , we see some evidence for the onset of diamagnetism in the 20–80 K range depending on composition and annealing conditions (figure 1). Details will be published shortly elsewhere.

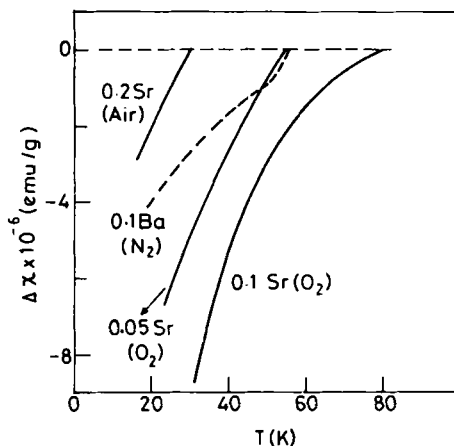


Figure 1. Diamagnetic contribution in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  showing onset in the 20–80 K range.

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