Superconductivity in layered nickel oxides

C N R RAO*, A K GANGULI and R NAGARAJAN
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India.

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Abstract. Likely presence of superconductivity in layered nickelates of K$_2$NiF$_4$ structure is pointed out.

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Since the discovery of superconductivity in La$_{2-x}$Ba$_x$CuO$_4$ 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$_x$CuO$_4$. La$_{2-x}$M$_x$CuO$_4$ (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$_2$CuO$_4$ and other transition metal oxides of K$_2$NiF$_4$ structure for some years (Ganguly and Rao 1984; Rao and Ganguly 1987). Thus, we have compared the properties of transition metal oxides of K$_2$NiF$_4$ structure especially those of the formula La$_{2-x}$Sr$_x$MO$_4$ (M = transition metal) with the corresponding three-dimensional perovskite oxides (Rao et al 1988).

Among these layered oxides, of special interest is La$_2$NiO$_4+\delta$ 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$_2$CuO$_4$ has an antiferromagnetic Neél temperature around 290 K (Mitsuda et al 1987) and shows an orthorhombic-tetragonal transition around 505 K.

La$_2$CuO$_4$ 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

*To whom all correspondence should be addressed.
La$_2$NiO$_{4-\delta}$ also there is a strong influence of the orthorhombic-tetragonal transition (~240 K) on the magnetic correlations in the paramagnetic state. Furthermore, the in-plane magnetic dynamics as well as the three-dimensional Neél temperature depend strongly on oxygen stoichiometry. It is clear that La$_2$NiO$_{4-\delta}$ is very similar to La$_2$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 La$_5$CuO$_{4+\delta}$ ($\delta > 0.0$), however, shows superconductivity (Beille et al 1987; Jorgensen et al 1988), but La$_2$NiO$_{4+\delta}$ does not.

La$_2$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 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 Ni$^{3+}$ (or oxygen holes) should show superconductivity at reasonably high temperatures.

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

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

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