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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 δ. For $\delta = +0{\cdot}001$, $\chi(T)$ 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 Neél 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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$La_2NiO_{4+\delta}$ also there is a strong influence of the orthorhombic-tetragonal transition ($\sim$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 $La_2NiO_{4+\delta}$ is very similar to $La_2CuO_{4+\delta}$ in most respects, the latter also showing a strong dependence of three-dimensional T_N on δ. Above T_N, there are two-dimensional magnetic correlations in both the oxides. Oxygen-excess $La_2CuO_{4+\delta}$ ($\delta > 0{\cdot}0$), however, shows superconductivity (Beille *et al* 1987; Jorgensen *et al* 1988), but $La_2NiO_{4+\delta}$ does not.

$La_2NiO_{4+\delta}$ 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 $La_2NiO_{4+\delta}$, the likely candidate for high T_c superconductivity would be oxides of the $Ln_{2-x}M_xNiO_{4+\delta}$ 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 $La_{n+1}Ni_nO_{3n+1}$ or (LaO) $(LaNiO_3)_n$ series of which La_2NiO_4 is the $n = 1$ member, does not help since it only makes the material metallic similar to $LaNiO_3$. A system such as $La_2SrNi_2O_{7+\delta}$ and $La_3SrNi_3O_{10+\delta}$ 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.

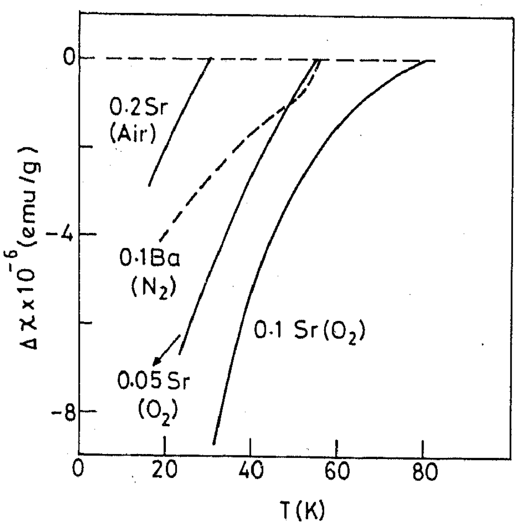

Figure 1. Diamagnetic contribution in $La_{2-x}M_xCuO_4$ showing onset in the 20–80 K range.

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