HIGH $T_c$ SUPERCONDUCTIVITY IN QUASI TWO-DIMENSIONAL COPPER OXIDES OF $K_2NiF_4$ STRUCTURE

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ABSTRACT

The highest superconducting critical temperature known till 1986 was 24 K, the $T_c$ increasing, on an average, by about 3 degree per decade since the 1920's. The discovery of high $T_c$ superconductivity in copper oxides of $K_2NiF_4$ structure (with $T_c$ close to 40 K) has opened new vistas. Marginal metallicity, low-dimensionality and mixed valence are some of the important features of these oxides.

$K_2NiF_4$ is a prototype, two-dimensional, antiferromagnetic insulator. The tetragonal structure of $K_2NiF_4$ consists of alternating layers of $KNiF_3$ perovskite layers and KF layers (figure 1), with no Ni-F-Ni interaction in the direction parallel to the c-axis\(^1\). Several oxides crystallize in structures related to $K_2NiF_4$ (figure 1) and some of them exhibit novel properties: crystal chemistry of oxides of the type $A_2BO_3$ has been examined in some detail by Ganguly and Rao\(^2\). Electrical and magnetic properties of these quasi two-dimensional oxides are quite different from those of the corresponding three-dimensional perovskites\(^3\). For example, $La_2NiO_4$ shows a metal-nonmetal transition in two dimensions\(^4\) around 500 K while $LaNiO_3$ is metallic with a resistivity of $\sim 10^{-3}$ ohm cm; $LaSrNiO_4$ is a semiconductor with a room-temperature resistivity of 0.1 ohm cm. Oxides of the type $La_1-xSr_1+xMnO_4$ possessing the $K_2NiF_4$ structure are paramagnetic semiconductors while the oxides $La_1-xSr_xMnO_3$ are itinerant-electron ferromagnets. Similarly, $La_1-xSr_xCoO_4$ compounds are paramagnetic insulators and the corresponding $La_1-xSr_xCoO_3$ becomes metallic and ferromagnetic above $x = 0.3$. In the SrO ($La_{0.5}Sr_{0.5}CoO_3$)\(_n\) system, both magnetization and electrical conductivity increase with the number of perovskite layers, $n$, approaching the value of the perovskite $La_{0.5}Sr_{0.5}CoO_3$. In general, the two-dimensional oxides exhibit considerably higher resistivity than the corresponding three-dimensional oxides\(^3\); there are similarly significant differences in magnetic properties.

$La_2CuO_4$ is an interesting oxide with an orthorhombic structure related to $K_2NiF_4$; this oxide shows a temperature-independent resistivity\(^5\) (1 ohm cm). $Pr_2CuO_4$ and $Nd_2CuO_4$, on the other hand, crystallize in a

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**Figure 1.** The $K_2NiF_4$ structure of the $A_2BO_3$ oxides.
tetragonal structure\(^2\) with \((\text{CuO}_2)\)^\(2^-\) and \((\text{Ln}_2\text{O}_2)\)^\(2^+/\) layers involving a four-fold coordination of Cu (instead of 6 as in \(\text{La}_2\text{CuO}_4\)). The last two oxides are high-resistivity materials\(^6\). Curiously, Cu\(^{2+}\) ions in these \(\text{Ln}_2\text{CuO}_4\) oxides do not contribute to the magnetic susceptibility at low temperatures\(^2,7\). Disproportionation of Cu\(^{2+}\) into Cu\(^{+}\) and Cu\(^{3+}\) has been considered to explain the magnetic properties.

None of the oxides of \(\text{K}_2\text{NiF}_4\) structure has been found to show true metallic conductivity\(^8\). However, partial substitution of La in \(\text{La}_2\text{CuO}_4\) by Sr or Ba makes the system nearly metallic. These quaternary oxides are the ones that show high \(T_c\) superconductivity\(^9,10\). Thus, \(\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4\) and \(\text{La}_{1.8}\text{Ba}_{0.15}\text{CuO}_4\) exhibit \(T_c\) of 36 K and 30 K respectively (figure 2). The high-temperature resistivity of these mixed valent oxides is close to the borderline value of resistivity in metal oxides at which the temperature coefficient of resistance changes sign\(^8,11\) (borderline of the metal-insulator transition). It is noteworthy that \(\text{LaSrCuO}_4\) and \(\text{La}_{2}\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4\) (with only Cu\(^{3+}\) ions) are insulators with the Cu\(^{3+}\) ions in the diamagnetic state.

A variety of systems related to \(\text{La}_{2-x}\text{Sr}_x\text{(Ba)}_x\text{CuO}_4\) offer themselves as candidates for high \(T_c\) superconductivity. Thus, we can examine the effect of chemical pressure as well as cation acidity on the \(T_c\) by suitably substituting for La and Sr in \(\text{La}_{1-x}\text{Sr}_x\text{CuO}_4\), noting that the application of hydrostatic pressure seems to increase \(T_c\). Accordingly, \(\text{La}_{1.8}\text{Sr}_{0.1}\text{Ca}_{0.1}\text{CuO}_4\) exhibits a \(T_c\) of 30 K (figure 2). Substitution of \(\text{Cu}\) by a small proportion of Ni brings down the \(T_c\) drastically. We are investigating the effect of substituting Sr and Ba by Pb.

Oxides of the type \(\text{La}_{2-x}\text{Ln}_x\text{CuO}_4\) (\(\text{Ln} = \text{Pr} \) or Nd) become stable in the \(\text{K}_2\text{NiF}_4\) (\(\text{La}_2\text{CuO}_4\)) structure\(^6\) beyond a critical value of \(x\). Our preliminary studies of \(\text{La}_{1-x}\text{Pr}_x\text{Cu}_y\text{O}_4\) have shown the \(T_c\) in these oxides to be in the 20–30 K range. \(\text{La}_{1.7}\text{Eu}_{0.25}\text{Sr}_{0.2}\text{CuO}_4\) also becomes superconducting in this range. It is noteworthy that high \(T_c\) in these copper oxides occurs in marginally metallic systems at the borderline of stability of the \(\text{K}_2\text{NiF}_4\) structure.

Bednorz and Müller\(^12\) suggested possible high \(T_c\) superconductivity in metallic, oxygen-deficient compounds of the type \(\text{Ba}_x\text{La}_{5-x}\text{Cu}_3\text{O}_{5(3-x)}\). It appears that superconductivity in such a system would really be due to the impurity\(^9\) of the two-dimensional \(\text{La}_{2-x}\text{Ba}_x\text{CuO}_4\). Low dimensionality appears to be necessary in addition to low metallicity (and mixed valency of copper). We find that three-dimensional \(\text{La}_4\text{BaCu}_3\text{O}_{13+x}\), which is really metallic\(^13\) (\(\sim 10^{-4} - 10^{-5}\) ohm cm resistivity) does not exhibit high \(T_c\) superconductivity. It may however be worthwhile to examine the effect of appropriate substitution of La and Ba ions in this oxide on superconductivity; we are now examining this system.

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NEWS

Albert Einstein World Award of Science for 1986

Dr M. S. Swaminathan, Director-General of the International Rice Research Institute at Los Baros, Philippines, has been awarded the 1986 'Albert Einstein' World Award of Science. The award is the highest recognition given to a scientist by the World Cultural Council. The committee consists of 120 world renowned scientists, including 20 Nobel Laureates.

The Award to Dr Swaminathan is in recognition of his contributions in the field of plant genetics which has been an important factor in the establishment of the Green Revolution in Asia in general and India in particular.

Dr Swaminathan served on the Working Committee of Current Science Association for more than ten years and took active interest in the growth and high standard of the Journal. Current Science Association is delighted to congratulate Dr Swaminathan on this occasion.