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_4 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[2,3]. 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 $La_{1-x}Sr_{1+x}MnO_4$ possessing the K_2NiF_4 structure are paramagnetic semiconductors while the oxides $La_{1-x}Sr_xMnO_3$ are itinerant-electron ferromagnets. Similarly, $La_{1-x}Sr_xCoO_4$ compounds are paramagnetic insulators and the corresponding $La_{1-x}Sr_xCoO_3$ 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.

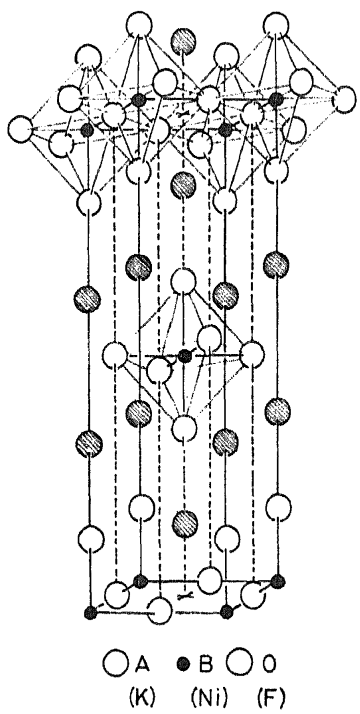

Figure 1. The K_2NiF_4 structure of the A_2BO_4 oxides.

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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tetragonal structure[2] with $(CuO_2)^{2-}$ and $(Ln_2O_2)^{2+}$ layers involving a four-fold coordination of Cu (instead of 6 as in La_2CuO_4). The last two oxides are high-resistivity materials[6]. Curiously, Cu^{2+} ions in these Ln_2CuO_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 K_2NiF_4 structure has been found to show true metallic conductivity[8]. However, partial substitution of La in La_2CuO_4 by Sr or Ba makes the system nearly metallic. These quarternary oxides are the ones that show high T_c superconductivity[9,10]. Thus, $La_{1.8}Sr_{0.2}CuO_4$ and $La_{1.85}Ba_{0.15}CuO_4$ 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 $LaSrCuO_4$ and $La_2Li_{0.5}Cu_{0.5}O_4$ (with only Cu^{3+} ions) are

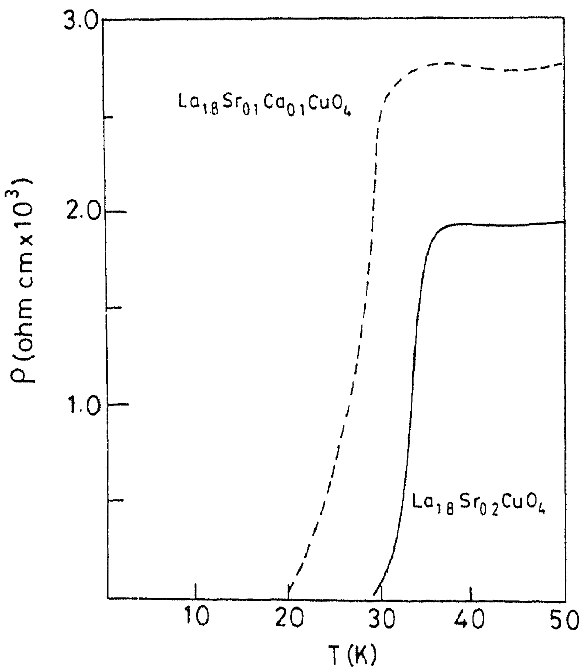

Figure 2. Temperature-variation of resistivity of two high T_c copper oxides.

insulators with the Cu^{3+} ions in the diamagnetic state.

A variety of systems related to $La_{2-x}Sr_x(Ba_x)CuO_4$ 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 $La_{1-x}Sr_xCuO_4$, noting that the application of hydrostatic pressure seems to increase T_c. Accordingly, $La_{1.8}Sr_{0.1}Ca_{0.1}CuO_4$ exhibits a T_c of 30 K (figure 2). Substitution of 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 $La_{2-x}Ln_xCuO_4$ (Ln = Pr or Nd) become stable in the K_2NiF_4 (La_2CuO_4) structure[6] beyond a critical value of x. Our preliminary studies of $(La_{1-x}Pr_x)_{2-y}Sr_yCuO_4$ have shown the T_c in these oxides to be in the 20–30 K range. $(La_{1.75}Eu_{0.25})_{1.8}Sr_{0.2}CuO_4$ 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 K_2NiF_4 structure.

Bednorz and Müller[12] suggested possible high T_c superconductivity in metallic, oxygen-deficient compounds of the type $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$. It appears that superconductivity in such a system would really be due to the impurity[9] of the two-dimensional $La_{2-x}Ba_xCuO_4$. Low dimensionality appears to be necessary in addition to low metallicity (and mixed valency of copper). We find that three-dimensional $La_4BaCu_5O_{13+x}$ 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.