planet in our Solar System is Jupiter and why there are none more massive is not understood. The lifetime of our gaseous proto-planetary disk may have been short[28] or the disk may have been tidally truncated by the growing planet itself[29]. Good statistics on the population of EGPs will better constrain proto-planetary disk processes. The absence of a Jupiter-class planet in a planetary system would imply a very different population of cometary-sized planetesimals than exists in our own Solar System, and this may have important implications for the origin, evolution and survival of life on rocky 'terrestrial' planets[30]. Only sensitive and systematic searches, such as those we anticipate over the next decade, will directly address these important issues of planet formation. ☐

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Superconductivity at 80 K in $(Sr,Ca)_3Cu_2O_{4+\delta}Cl_{2-y}$ induced by apical oxygen doping

C.-Q. Jin*, X.-J. Wu, P. Laffez†, T. Tatsuki, T. Tamura, S. Adachi, H. Yamauchi†, N. Koshizuka & S. Tanaka

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
10-13 Shinonome, 1-Chome, Koto-ku, Tokyo 135, Japan

RECENT work[1,2] has shown that superconducting copper oxyhalides can be synthesized, with the La_2CuO_4 structure but with no oxygen in the 'apical' positions outside the CuO_2 planes. For these materials to be rendered superconducting, charge carriers must be introduced into the CuO_2 planes; in previous work, positive carriers (holes) have been introduced by the incorporation of interstitial fluorine in $Sr_2CuO_2F_{2+\delta}$ (transition temperature $T_c = 46$ K)[1], or by the substitution of sodium for calcium in $(Ca,Na)_2CuO_2Cl_2$ ($T_c = 26$ K)[2]. Here we present an alternative doping approach for this copper oxyhalide family: holes are introduced by partially replacing the (monovalent) halogen that occupies the apical sites with (divalent) oxygen. We have obtained bulk superconductivity with T_c above 77 K in a new double-layer compound $(Sr,Ca)_3Cu_2O_{4+\delta}Cl_{2-y}$, which is isostructural with $(La,Sr)_2CaCu_2O_6$ (ref. 3), with (Sr,Ca) at the (La,Sr) or Ca sites, and Cl at the apical sites outside the CuO_2 planes.

We synthesized $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$ compounds using a high-pressure, high-temperature technique, which has proven effective in searching for new homologous series of high-T_c superconducting copper oxides[4–6]. The precursors Sr_2CuO_3, $SrCuO_2$ and Ca_2CuO_3 were prepared by solid-state reaction between CuO and $SrCO_3$ or $CaCO_3$ (each 99.9% pure). Precursor $Sr_2CuO_2Cl_2$ (Cl source of the sample) was obtained by the reaction between CuO and fully dehydrated $SrCl_2$ (99% pure) at 800 °C in flowing O_2. The precursors were mixed, in an argon-filled glove box, with SrO_2 (99% pure) and CuO powders in a stoichiometry of $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$ with 10% excess CuO. The materials were then subjected to high-pressure synthesis at 5.0 GPa at ~1,000 °C for 1 h using a cubic-anvil-type high-pressure apparatus. Adding excess CuO, which in most cases remained an impurity in the final products, to the starting materials was found to enhance the formation of the phase $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$. The role of SrO_2 is to create an oxygen atmosphere during the high-pressure synthesis, with the oxygen pressure controlled by the amount of SrO_2 in the nominal starting composition. In the absence of SrO_2, the $Sr_{3-x}Ca_xCu_2O_4Cl_2$ product is an insulator.

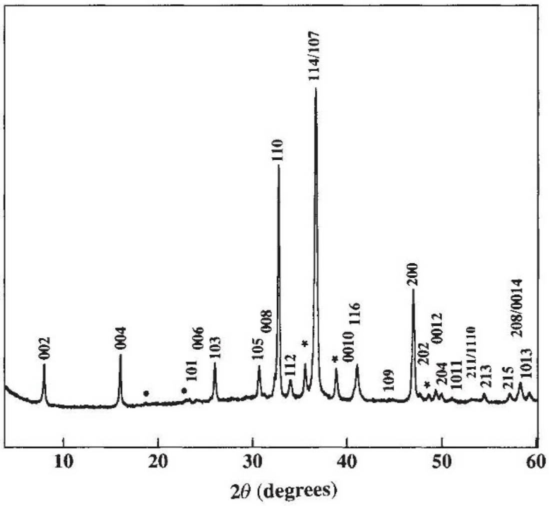

FIG. 1 X-ray powder diffraction pattern of $Sr_{2.3}Ca_{0.7}Cu_{2.0}O_{4+\delta}Cl_{1.3}$. Main peaks are assigned to a tetragonal structure (space group *I4/mmm*) with $a = 3.87$ Å and $c = 22.16$ Å. Also indicated are peaks from CuO impurity (*), and from unidentified minor phase(s) (●).

By using a 0.4 molar ratio of SrO_2 in the nominal starting composition, we synthesized superconducting samples with the predominant phase being $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$ for $0 \leq x \leq 1.0$ and $0.40 \leq y \leq 0.80$, as shown by the X-ray powder diffraction pattern in Fig. 1 for $Sr_{2.3}Ca_{0.7}Cu_{2.0}O_{4+\delta}Cl_{1.3}$. As expected, the

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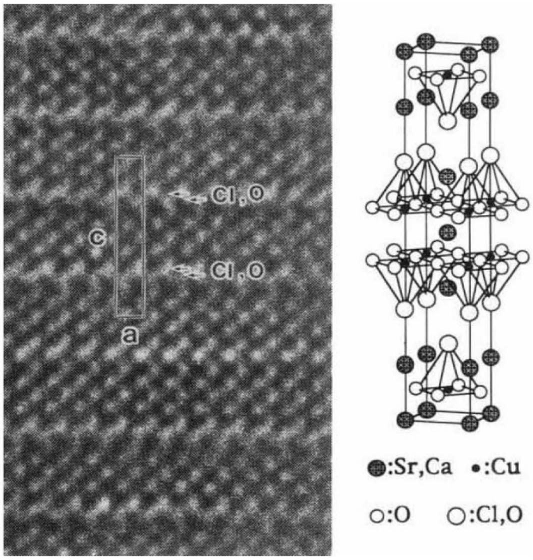
* Permanent address: Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.

† Present addresses: Surfaces et Supraconducteurs CNRSUPR5 ESPCI 10, Rue Vauquelin 75231, Paris, France (P.L.); Center for Ceramics Research, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan (H.Y.).

sample also contained CuO and unidentified minor phase(s). We did not find any evidence from powder diffraction for other superconducting phases in these samples, such as $(Sr,Ca)_{n+1}Cu_nO_{2n+1+\delta}$ (refs 4, 7, 8), which can be formed at high pressure from the same cation-forming elements used here.

We determined the crystallography, microstructure and compositions of our samples using X-ray powder diffraction, high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) using a scanning electron microscope. $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$ crystallizes in a tetragonal structure, with space group *I4/mmm*. It is isostructural with $(La,Sr)_2CaCu_2O_6$, (ref. 3) with (La,Sr) or Ca replaced by (Sr,Ca), and with the apical oxygens replaced by Cl. Crystallographically, $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$ constitutes the $n=2$ member of a new homologous series $(Sr,Ca)_{n+1}Cu_nO_{2n}Cl_2$, with $Sr_2CuO_2Cl_2$ (refs 9, 10) being the $n=1$ member. As a result, in the ideal case of $Sr_{3-x}Ca_xCu_2O_4Cl_2$, all the apical oxygens of the CuO_2 planes are thus replaced by Cl. In our superconducting samples, however, EDS analysis (using $Sr_2CuO_2Cl_2$ as a reference material) reveals that the Cl content in the $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$ grains is significantly less than 2. The average Sr:Ca:Cu:Cl atomic ratio over tens of well grown $Sr_{2.3}Ca_{0.7}Cu_2O_{4+\delta}Cl_{1.3}$ grains is approximately 34:14:32:20, in agreement with the suggested formula of the new compound. This result suggests that there is insufficient Cl to fully occupy the apical site. As the samples were synthesized under a high oxidizing pressure, it is reasonable to assume that a few oxygens are in turn incorporated in the apex site. The increase of *c*-axis length on going from $Sr_{2.3}Ca_{0.7}Cu_2O_4Cl_2$ ($a=3.89$ Å, $c=22.02$ Å) to $Sr_{2.3}Ca_{0.7}Cu_2O_{4+\delta}Cl_{1.3}$ ($a=3.87$ Å, $c=22.16$ Å) can be explained by the expansion of the (Sr,Ca)–Cl rock-salt block due to enhanced Coulomb repulsion between the adjacent (monovalent) Cl layers resulting from the introduction of (divalent) oxygen. The reduction of the *a* dimension is expected for p-type carrier doping. Similar to the observation[9,10] in $Sr_2CuO_2Cl_2$, the large Cl^- ion ($r(Cl^-)=1.81$ Å)[11] leads to highly puckered (Sr,Ca)–Cl rock-salt layers as shown by the HRTEM image in Fig. 2*A*. Following the crystal structure model illustrated in Fig. 2*B*, we performed an X-ray Rietveld refinement for $Sr_{2.3}Ca_{0.7}Cu_2O_{4+\delta}Cl_{1.3}$. The chlorine occupancy at the apical site was considered as a variable, with the rest of this site being assumed to be substituted by oxygen. Table 1 summarizes the refinement results. The refinement gave a weighted-profile *R*-factor of 5.69%, indicating that the structural model is a reasonable one. The refined composition, $Sr_{2.3(5)}Ca_{0.7(5)}Cu_{2.0}O_{4.8(4)}Cl_{1.2(4)}$, is in reasonable agreement with the proposed formula for the new compound. However, because both EDS and X-ray Reitveld refinement are not sensitive to light elements such as oxygen in the crystal structure, the analysis performed here has large systematic error. These preliminary results should therefore be confirmed by other more precise measurements, such as neutron diffraction.



A *B*

FIG. 2 *A*, Typical high-resolution transmission electron microscopy image taken along [100] in $Sr_{3-x}Ca_xCu_{2.0}O_{4+\delta}Cl_{2-y}$ samples, revealing a long periodicity along the *c* direction. The excess oxygen was presumed to occupy the vacancy at the chlorine site. Due to the large ionic radius of Cl^- (1.81 Å)[11], (Cl, O) layers concomitantly shift away from the CuO_2 sheets, leading to a very puckered (Sr,Ca)–(Cl,O)–(Cl,O)–(Sr,Ca) rock-salt block. *B*, Schematic view of the crystal structure of $Sr_{3-x}Ca_xCu_{2.0}O_{4+\delta}Cl_{2-y}$, which is isostructural with $(La,Sr)_2CaCu_2O_6$, where (La,Sr) or Ca has been replaced by (Sr,Ca), and apical oxygens of the CuO_2 pyramidal planes have been replaced by Cl.

TABLE 1 Crystallographic data for $Sr_{2.3}Ca_{0.7}Cu_2O_{4+\delta}Cl_{1.3}$

Atom	Site	*x*	*y*	z	Occupancy	B_{iso} (Å^2)
(Sr/Ca) (1)	2a	0	0	0	0.5/0.5 (3)	3.0/1.0
(Sr/Ca) (2)	4e	0	0	0.1507 (8)	0.9/0.1 (2)	2.0/1.0
Cu	4e	0	0	0.428 (1)	1.0	1.0
O (1)	8g	0.5	0	0.428 (1)	1.0	3.0
O (2)	4e	0	0	0.31 (2)	0.38 (18)	2.0
Cl	4e	0	0	0.298 (8)	0.62 (18)	3.0

Space group, *I4/mmm*: unit-cell dimensions; $a=b=3.8679$ (2) Å, $c=22.161$ (1) Å: $R_{wp}=5.69\%$, $R_p=4.22\%$, $R_e=2.78\%$, $R_i=4.49\%$, $R_f=3.19\%$, where R_{wp}, R_p, R_e, R_i and R_f are the *R*-factors for the weighted-profile, profile, expected, integrated intensity and structure factor of the fit, respectively. Cu Kα radiation was used; the refinement range of 2θ was 25–110°. Values in parentheses represent the standard deviation in the last digit; B_{iso} is the isotropic thermal parameter; the total occupancy at each site of (Sr/Ca) (1), (Sr/Ca) (2) and Cl/O (2) was fixed as 1; the CuO_2 (1) was constrained to a plane.

We characterized the superconducting properties of the samples by measuring the d.c. susceptibility using a SQUID magnetometer and the d.c. resistivity by the four-probe method. The superconducting samples typically have T_cs of 60–80 K and large Meissner volume fractions (>20% at 5 K). Figure 3 shows that $Sr_{2.3}Ca_{0.7}Cu_2O_{4+\delta}Cl_{1.3}$ undergoes a superconducting transition at 80 K. The Meissner volume fraction of 35% indicates bulk superconductivity. In reality, the sample is not single-phase, as revealed by the powder diffraction pattern. However, as no systematic correlation between the Meissner volume fractions and the amount of impurity phase(s) was found in the superconducting samples, it is reasonable to assign the superconducting transition to the $Sr_{3-x}Ca_xCu_2O_{4+\delta}Cl_{2-y}$. This transition temperature is much higher than the 60-K T_c of $(La,Sr)_2CaCu_2O_6$ (ref. 3), and is the highest T_c yet reported for a copper oxyhalide superconductor. The Fig. 3 inset shows the temperature dependence of the sample resistivity. The higher T_c^{onset} of ~90 K and the wider transition range in the resistivity data may imply that the sample is chemically inhomogeneous.

It is believed that a requirement for superconductivity in the layered copper oxides is the creation of charge carriers by either oxidizing (hole-doping) or reducing (electron-doping) the CuO_2 planes. The presence of the strong oxidizing atmosphere during our synthesis and the aforementioned lattice-parameter evolution suggest that these copper oxyhalide superconductors are hole-doped. The doping cannot be due to cation substitution[2] because Sr and Ca cations are isovalent, and is not likely to be due to interstitial anions[1] either, as we will discuss below. We suggest, instead, that the substitution of oxygen for (apical) Cl may provide a new hole-doping mechanism, 'apical oxygen doping'. Using the formula given by the Rietveld refinement, the charge balance resulting from the apical oxygen complement gives a hole concentration of up to 0.4 (2) per CuO_2 unit. The hole concentration for an optimized p-type high-T_c supercon-

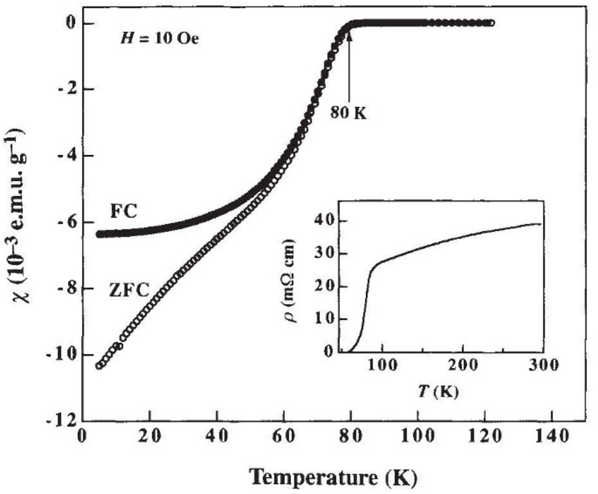


FIG. 3 Temperature dependence of d.c. magnetic susceptibility of $Sr_{2.3}Ca_{0.7}Cu_{2.0}O_{4+\delta}Cl_{1.3}$. The measurement was carried out using a d.c. SQUID magnetometer (Quantum Design) in both zero-field cooling (ZFC) and field cooling (FC) mode in a 10-Oe field. A bulk superconducting transition is observed at 80 K, with a Meissner volume fraction of 35%. Inset, resistivity as a function of temperature measured by the four-probe method with a 0.1-mA current.

ducting copper oxide usually[12] ranges from 0.12 to 0.25. If this 'rule' holds here, in principle apical oxygen doping is able to contribute sufficient carriers to support p-type superconductivity (perhaps a few vacancies at the apical site would lead to optimum doping).

In the Rietveld refinement we ignored the possibility of interstitial anions—a source of hole carriers known from other La_2CuO_4-type materials[1,13]. The most likely 'interstitial' site in this double-layer structure is the open 2b site in the Sr/Ca(1) spacer layer interleaved between the two adjacent pyramidal CuO_2 planes. The site (an apical position relative to the CuO_2 planes) is vacant in the ideal structure[14]. In view of the highly oxidizing condition and the ion size (1.40 Å for O^{2-}, and 1.81 Å for Cl^- (ref. 11), the probable interstitial anion here would be oxygen. But the incorporation of oxygen at this site in $(La,Sr)_2CaCu_2O_{6-\delta}$ (ref. 15) is known to suppress superconductivity suggesting that this 'interstitial' anion should not exist, or play a positive role in the present superconducting phase. Thus apical oxygen doping, a partial substitution of divalent oxygen for the monovalent apical halogen, appears the most plausible p-type carrier doping mechanism for this double-layer copper oxyhalide superconductor. This is the first time that p-type carrier doping has been achieved through anionic ion (not ion cluster[16]) substitution, analogous to the well established cation substitutions used in other high-T_c superconducting copper oxides.

There accordingly seems to be at least three carrier doping routes leading to p-type superconducting copper oxyhalides: interstitial halogen insertion[1], cation substitution[2] and anion substitution (this work). The significance of the present approach is that it has distinguished the effectiveness of apical oxygen as a dopant for oxidizing the CuO_2 plane for otherwise apical-oxygen-free materials. Apical oxygen doping (or its joint use with the other two mechanisms) may lead to further multilayer high-T_c copper oxyhalide superconductors. ☐

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Synthetic molecules that fold into a pleated secondary structure in solution

R. Scott Lokey & Brent L. Iverson*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA

THE construction of synthetic molecules that fold or assemble predictably into large, well defined structures represents a fertile area of chemistry. Many supramolecular systems have been reported that self-assemble as a result of non-covalent interactions[1–7]; and the control of higher-order protein structure by *de novo* design has also been demonstrated[8,9]. Protein secondary structural motifs have also been stabilized by incorporating artificial groups that impose constraints on the folded architecture[10–12]. Here we describe the synthesis of molecules that will fold in water into a pleated structure, as a result of interactions between alternating electron-rich donor groups and electron-deficient acceptor groups. We verify the pleated structure using absorption and NMR spectroscopy. Donor–acceptor interactions have been used previously to engineer specific supramolecular geometries[2,13], and are energetically favourable in organic as well as in aqueous solutions. But whereas previously such interactions have been used to effect self-assembly of distinct molecules, our results show that they can also determine the secondary structure of complex synthetic molecules in solution.

Our system incorporates 1,5-dialkoxynaphthalene and 1,4,5,8-naphthalenetetracarboxylic diimide (Fig. 1*a*) as aromatic donor and acceptor units, respectively. These moieties were chosen because they are readily functionalizable, and their donor–acceptor complex is relatively stable in aqueous solution. For example, monomers **1** and **2** have an association constant of 130 M^{-1} in water, as determined by standard NMR[14] and ultraviolet–visible[15] spectroscopic analysis.

Our aim was to assemble the donor and acceptor groups on a suitable backbone such that they would stack to give a pleated structure (Fig. 1*b*). To assist in design of an appropriate backbone, we obtained an X-ray structure of the co-crystal between the monomers **3** and **4** (Fig. 2). Taking this alignment of the rings as a probable energy minimum in solution, molecular mechanics simulations predicted that the backbone shown in Fig. 1*c* would be compatible with the stacked structure of the co-crystal, folding to give the secondary structure shown in Fig. 1*d*. In theory, any α-amino acid could be placed between the 1,5-dialkoxynaphthalene and 1,4,5,8-naphthalenetetracarboxylic diimide groups. Initially, we have chosen L-aspartic acid residues for the backbone so as to increase water solubility and prevent aggregation. The series **5–7** (Fig. 1*c*) was synthesized by solid-phase methods, and below we report spectroscopic evidence consistent with the

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* To whom correspondence should be addressed.