A different branch of the high T_c family?

D. J. Scalapino[a,1]

In PNAS, Li et al. (1) suggest that Ba_2CuO_{4-y} is a member of a different branch of high-T_c cuprate superconducting materials. This branch is characterized as heavily overdoped with an exceptionally short Cu apical O spacing and O vacancies that are located in the CuO_2 planes. These characteristics, illustrated in Fig. 1, differ in significant ways from those of the traditional cuprate superconducting materials (2).

For example, consider $La_{2-x}Sr_xCuO_4$ (LSCO), which has the same K_2NiF_4 structure as Ba_2CuO_{4-y}. Using a valence count with La^{+2}, Sr^{+3}, and O^{-2}, the number of holes in the Cu 3*d* shell of LSCO is $1+x$. For $x=0$, LCO is antiferromagnetic. As Sr is added the antiferromagnetic Néel temperature decreases as shown in Fig. 1*A* and superconductivity onsets with T_c peaking at a small doping $x \sim 0.15$. At larger doping, as the system moves further away from the antiferromagnetic Mott–Hubbard phase, T_c decreases and vanishes for $x > 0.25$. For Ba_2CuO_{4-y}, the valence of Ba is +2 so that the hole doping $x = 2(1-y)$. Thus, the $y = 0.8$ sample Li et al. (1) discuss is heavily overdoped with $x = 0.4$. Nevertheless, the T_c of Ba_2CuO_{4-y} is approximately 30 K higher than that of optimally doped LSCO.

Like the previously reported highly overdoped cuprate materials (3–8) Sr_2CuO_{4-y}, $(Sr,Ba)_2CuO_{4-y}$, and $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7.54}$, Ba_2CuO_{4-y} is synthesized under high pressure and high temperature in the presence of a strong oxidizing agent. While the crystal has the K_2NiF_4 structure illustrated in the center of Fig. 1*B*, the CuO_6 octahedron structure is highly compressed with a much shorter Cu–O apical distance (1.86 Å) than the traditional cuprates (2.42 Å for La_2CuO_4). This is schematically illustrated at the left and right in Fig. 1*B*. The shortening of the Cu–O apical distance raises the energy of the $3d_{3z^2-r^2}$ orbital so that in Ba_2CuO_{4-y} the Cu states near the Fermi level have both $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ orbital character. As the authors note, a shortened apical Cu–O distance and the admixing of $3d_{3z^2-r^2}$ orbital weight in the states near the Fermi energy are found to reduce T_c in the traditional cuprate superconductors (9).

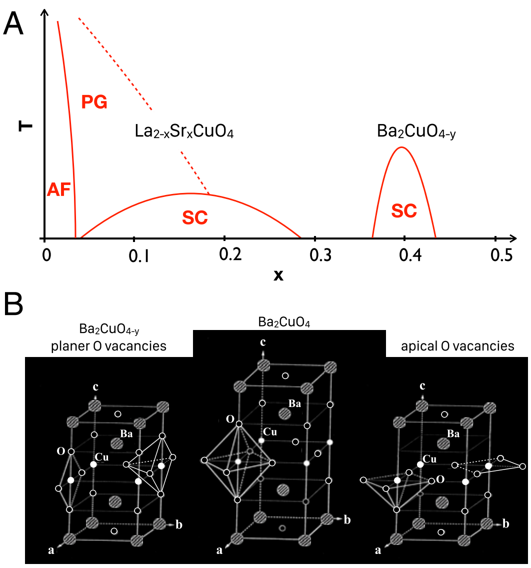

Fig. 1. (*A*) A schematic cuprate phase diagram as a function of hole doping *x*. On the left at low doping are the familiar antiferromagnetic (AF), pseudogap (PG), and *d*-wave superconducting (SC) regions of $La_{2-x}Sr_xCuO_4$. On the right is the heavily overdoped $x \sim 0.4$ region of superconductivity Li et al. (1) discuss for Ba_2CuO_{4-y}. (*B*) The center panel shows a fictitious Ba_2CuO_4 compound with the same K_2NiF_4 structure as La_2CuO_4. The structures shown on the left and right have the compressed *c*-axis structure of Ba_2CuO_{4-y}. In this case the hole doping is controlled by the O vacancies. For the structure on the right, the O vacancies are on the apical sites and the CuO_4 corner-shared CuO_2 sheets remain intact. However, according to Li et al. (1) in Ba_2CuO_{4-y} the O vacancies are in the plane. In this case, as shown by the structure on the left, the CuO_2 sheets are destroyed and randomly oriented Cu–O chain segments are likely formed.

Finally, the authors note at the end of the legend for figure 3 in ref. 1 that while the exact positions of the O vacancies are not known at present, they are in the CuO_2 planes. This agrees with the conclusions of Geballe and Marezio (5) regarding the O vacancies in Sr_2CuO_{4-y}. A number of earlier studies Li et al. (1) cite assume that the oxygen vacancies were at the apical O sites. In this

[a]Department of Physics, University of California, Santa Barbara, CA 93106
Author contributions: D.J.S. wrote the paper.
The author declares no conflict of interest.

See companion article on page 12156.
[1]Email: djs@physics.ucsb.edu.
Published online June 4, 2019.

case, while there would be CuO_5 pyramidal structures and square fourfold coordinated CuO_4 along with the CuO_6 octahedral units, the CuO_2 planes would survive intact as illustrated in the right-hand structure of Fig. 1*B*. However, if the oxygen vacancies are in the CuO_2 planes one will have Cu–O chain structures rather than the CuO_2 planes as indicated in the left-hand structure of Fig. 1*B*. The 2D CuO_2 planes, consisting of corner-shared CuO_4 units, are considered the key structural elements of the traditional cuprate superconductors. They are the defining characteristic of these superconductors and imperfections in these layers are known to reduce T_c.

As noted, Ba_2CuO_{4-y} is made under high pressure and temperature resulting in polycrystalline samples and the precise location of the oxygen vacancies in the CuO_2 plane remains open. Nevertheless, the remarkably high T_c of this highly overdoped cuprate with its short Cu apical O separation and its O vacancies in the CuO_2 plane suggest that it is a member of a different branch of high-T_c cuprate materials, which challenges the basic tenants of many high-T_c theories.

Acknowledgments

I thank Thomas Maier and Tom Berlijn for their help with the figure and for useful discussions. This work was supported by the Scientific Discovery through Advanced Computing (SciDAC) program funded by the US Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences, Division of Materials Sciences and Engineering.

1 W. M. Li *et al.*, Superconductivity in a unique type of copper oxide. Proc. Natl. Acad. Sci. U.S.A. **116**, 12156–12160 (2019).
2 S. K. Gupta, H. Jangam, N. Sharma, Review of high temperature superconductors and application in various fields. *Res. Dev. Mater Sci.* **7**, 000668 (2018).
3 Z. Hiroi, M. Takano, M. Azuma, Y. Takeda, A new family of copper oxide superconductors $Sr_{n+1}Cu_nO_{2n+1+\delta}$ stabilized at high pressure. *Nature* **364**, 315–317 (1993).
4 Q. Q. Liu *et al.*, Enhancement of the superconducting critical temperature of $Sr_2CuO_{3+\delta}$ up to 95 K by ordering dopant atoms. *Phys Rev B* **74**, 100506(R) (2006).
5 T. H. Geballe, M. Marezio, Enhanced superconductivity in Sr_2CuO_{4-y}. *Physica C* **469**, 680–684 (2009).
6 W. B. Gao *et al.*, Out-of-plane effect on the superconductivity of $Sr_{2-x}Ba_xCuO_{3+\delta}$ with $T_c$up to 98 K. *Phys. Rev. B* **80**, 094523 (2009).
7 Y. Liu *et al.*, A new modulated structure in $Sr_2CuO_{3+\delta}$ superconductor synthesized under high pressure. *Physica C* **497**:34–37 (2014).
8 A. Gauzzi *et al.*, Bulk superconductivity at 84 K in the strongly overdoped regime of cuprates. *Phys. Rev. B* **94**, 180509 (R) (2016).
9 E. Pavarini *et al.*, Band-structure trend in hole-doped cuprates and correlations with Tcmax. *Phys. Rev. Lett.* **87**, 047003 (2001).