This Week's Citation Classic®

Ovshinsky S R, Young R T, Allred D D, DeMaggio G & Van der Leeden G A.
Superconductivity at 155 K. *Phys. Rev. Lett.* 58:2579-81, 1987.
[Energy Conversion Devices, Inc., Troy, MI]

Transition to a superconducting zero-resistance state at 155 K is observed for the first time in bulk material. A new five-element multiphasic compound has been synthesized with nominal composition $Y_1Ba_2Cu_3F_2O_y$. Fluorine plays a critical role in achieving this effect. [The *SCI*® indicates that this paper has been cited in over 130 publications.]

Zero Resistance at 155 K and Above

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My scientific interest in superconductivity accelerated with the first papers on the A-15 compounds that assumed crystallinity was crucial. I felt what was described were nonequilibrium materials in which short-range order and metastability and disorder played an important role. I therefore developed amorphous materials to demonstrate that A-15 crystallinity was not only not necessary, but that there were advantages to the amorphous state. I showed that amorphous films could have orders of magnitude higher critical field capability than had been reported until then—over 150 kG—so high there was no equipment to measure it. The superconductivity was a very respectable zero resistance at 9 K.[1]

In the late 1970s, Morrell Cohen suggested that we look into copper chloride materials for which reports had indicated that anomalous, fleeting superconductivity could be observed. The reason he knew this would be of interest to me was that in the 1950s and in 1960 I had worked on transition metal oxides (including copper oxide) that showed extreme drops of electrical resistance in response to either an electric field or, in the case of copper oxide, to heat. In the 1970s, I thought of many approaches that led to multilayered thin-film devices, which showed unusual superconducting properties.[2]

When the new high-temperature superconductors were announced, I immediately got a small group together, headed by my collaborator Dr. Rosa T. Young, to investigate how my previous approaches to fluorine chemistry, local order, metastability, amorphicity, disorder, and defects could be utilized to stabilize materials and increase the transition temperature by making new materials. I had successfully utilized fluorine in our work in photovoltaic amorphous materials and felt that its small size, extreme electronegativity (being a "super" halogen) would make it an ideal addition and replacement for the oxygen systems being used. Following a mixed valence model (where mobile antiferromagnetic pairs played an important role) that I was developing with my colleagues,[3,4] I felt that fluorine would allow me to change the charge balance, permit the addition of other chemical compensators, as well as play both a beneficial structural and electronic role. We made such devices and were able to show 150-168 K high-temperature superconductivity. (It is interesting that we later saw in materials of even less stability T_cs between 200 and 309 K with even larger Meissner effects but did not report in detail on them because of their lack of reproducibility.)

All of our devices, however, were multiphasic and the conducting percolation path was so fragile that the effect would not last more than three days under cycling conditions. Having repeated the results by postfluorination plasma treatment,[5] we knew that the phenomenon was there. We also received reports from several other researchers who, after reading our paper, utilized fluorine and got similar results (see, for example, references 6 and 7). The lack of reproducibility led us to a method of inserting fluorine in a nonequilibrium manner that indicates that we will be able to make single phase materials that should be reproducible.

Fluorine makes for a much more stable material, limits oxygen diffusion, and aligns crystallites perfectly so that microcrystalline materials can be used without creating bottlenecks to current flow. These proven and reproducible solutions to major problems indicate that fluorinated materials (which can be either hole- or electron-mobility-dominated), coupled with our understanding of local relationship and defects from our amorphous work, create exciting prospects for making very high-temperature stable materials capable of conducting substantial superconducting currents on more suitable substrates. They have shown tantalizing potential for higher than 200-300 K transition temperatures.

[Editor's note: An earlier paper by Dr. Ovshinsky has also appeared as a *Citation Classic*.[8]]

1. Internal Energy Conversion Devices, Inc. reports, 1975 and 1977. Original samples remeasured at the Francis Bitter National Magnet Lab. Report dated July 1982-June 1983. p. 118.
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3. **Ovshinsky S R, Hudgens S J, Lintvedt R L & Rorabacher D B.** A structural chemical model for high T_c ceramic superconductors. *Mod. Phys. Lett. B* 1:275-88, 1987. (Cited 5 times.)
4. **Ovshinsky S R.** An answer to the puzzle of high-temperature superconductivity: a letter to David Adler. (Adler D, Schwartz B B & Silver M, eds.) *Disordered materials: science and technology—selected papers by S.R. Ovshinsky.* New York: Plenum Press. (In press.)
5. **Young R T, Ovshinsky S R, Chao B S, Fournier G & Pawlik D.** Superconductivity in the fluorinated YBaCuO. *Mater. Res. Soc. Symp. Proc.* 99:549, 1988.
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7. **Bhargava R N, Herko S P & Osborne W N.** Improved high-T_c superconductors. *Phys. Rev. Lett.* 59:1468-71, 1987. (Cited 80 times.)
8. **Ovshinsky S R.** Reversible electrical switching phenomena in disordered structures. *Phys. Rev. Lett.* 21:1450-3, 1968. (Cited 550 times.) [See also: **Ovshinsky S R.** Citation Classic. (Thackray A, comp.) *Contemporary classics in physical, chemical, and earth sciences.* Philadelphia: ISI Press, 1986. p. 97.]

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