Research advances into Mercury compounds for superconductors

by Mark Wilsey

In 1911 Dutch physicist Heike Kamerlingh Onnes discovered the first superconductor, mercury. Now more than 80 years later, French scientists have discovered a new family of mercury compounds which are the highest transition temperature superconductors yet found. Researchers at the National Center for Scientific Research (CNRS) in Grenoble found these compounds last year. The research has been led by Massimo Marezio at the CNRS Laboratory of Crystallography and Jean-Louis Tholence from the CNRS Center for Cryogenic Research.

However, the work on mercury surperconductors orginated with Yevgeni Antipov and Sergei Putilin, two scientists from the Moscow State University. According to Marezio, this collaboration started when he was invited to a workshop in Moscow by the chemistry department of the State University. There he became interested in a paper by Antipov and Putilin, who are experts in the very specific chemistry of mercury, about a mercury compound which had all the features of a superconductor, but was not a superconductor. Antipov and Putilin started with yttrium-barium-copper oxide (known as YBCO) and tried replacing one copper atom with mercury to get YBa_2HgCu_2O. They also tried replacing yttrium with other rare earth compounds, but were unable to find any sign of superconductivity in all these compounds. In order to continue the investigation as to why these compounds were not superconducting, Marezio invited Antipov and Putilin to come to Grenoble. It was there that the team made the superconducting mercury compounds.

The reason Russian compounds didn't work, it was speculated, was that the charge of the copper was too small. Jean Tholence explained to me that it is an empirical rule of thumb that the charge of the copper must be around 2.3 to have superconductivity. The first idea was to reduce yttrium, to make $HgBa_2CuO$, which was found to be superconducting at 98 Kelvin. The second idea was to replace yttrium with calcium to raise the valence of the copper. Introducing calcium gave a new family of mercury compounds. The compounds are made up of mercury, barium, calcium, and copper oxides of the general form $HgBa_2Ca^{n-1}Cu^nO$, where n=1, 2, 3. This yields the following shorthand, Hg-1201, Hg-1212, and Hg-1223, denoting the number of calcium atoms and copper oxide layers in the compounds. The latter two were found to be superconducting at 128 K and 135 K, which was confirmed by a research team in Zurich.

These are the three mercury compounds that have been isolated and studied so far, although others are known to exist. "We now have phases with Hg-1234, Hg-1245," Tholence told me, "but up to now the T_c is not optimized." For compounds with higher numbers of copper-oxygen layers, the T_c seems to decrease somewhat. For example, the phase Hg-1256 could have a T_c around 100 K.

As a group, these mercury compounds lead the pack of other superconductors with the highest T_c of any copper-oxide layered compound of two or three layers. James Jorgensen, a researcher at Argonne National Laboratory in Illinois, who has been following this work with interest, observes that "the remarkable thing in these new compounds is that their structures are really very simple, simpler than the thallium and bismuth structures that previously held the record for the highest critical temperatures."

The high T_c superconductors are based on layered copper-oxide structures with another kind of layer which modifies in chemistry to control the electronic structure. Previously these have been made with thallium or bismuth.

Robert Hazen of the Carnegie Institution of the Washington Geophysical Laboratory has recently completed the first single crystal X-ray studies of the crystal structures of these mercury compounds. He finds the mercury-based superconductors to have the same structure as the thallium superconductors. The 1223, 1212, and 1021 structures, which occur in thallium-based systems, are well known. "These are not new structure types, but they are new compositional variants of that structure type," Hazen said. Hence, when Jorgensen describes the structure of these mercury compounds as being "relatively simple," he is pointing out that they lack features which make other systems more complicated. E.g., in the bismuth and thallium materials, there are chemical substitutions and displacements of atoms which make them more difficult to understand.

The difference is that the mercury is only strongly connected to two oxygen atoms. "In between the copper-oxygen planes there are mercury planes," explained Tholence. "And since there are only two bonds between mercury and oxygen, then there is no problem in arranging the structure over long distances." In other words, there is less force from chemical bonds to deform the structure, allowing the mercury planes to remain flat.

The mercury compounds are fabricated under pressure, with the synthesis being made at between 20,000 and 80,000 atmospheres. The process and equipment are similar to those used to make artificial diamonds. In the case of these mercury compounds, the high pressure is needed to control the formation reaction. In addition, the process seems to yield samples of a fairly uniform phase and not mixtures of phases with differing compositions, as with other materials.

The compounds are made by mixing a precursor which contains barium, copper and calcium-oxides, and mercury-oxides. If the pressure is not high enough, the mercury-oxide decomposes, and does not react. Whereas under high pressure, the decomposition temperature of mercury-oxide is raised enough such that, around 800 C, the temperature at which the process operates, the mercury-oxide does not decompose and can react to produce the desired product.

As if holding the world record for the highest T_cs were not enough, these materials soon showed they could pull off another interesting feat: The T_c of these materials could be increased under pressure. For example, the three-layered compound Hg-1223 has a T_c of 135 K; however, when roughly a quarter-million atmospheres of pressure is applied, the T_c rises to 165 K, another 30°. Paul Chu's team at the Texas Center for Superconductivity at the University of Houston was the first to reproduce this high-pressure work, in experiments that were conducted at about the same time as those in Grenoble. Within a week, the two laboratories were able to confirm each other's findings. Now, Japanese scientists at the International Superconductivity Technology Center (ISTEC) and others have also repeated it.

Although there is no practical application for superconductivity at those pressures, its achievement tells us that superconductivity does exist at those temperatures. According to Jorgenson, this achievement opens up the field for trying to attain superconductivity at high temperatures without the application of pressure by means of appropriate chemical substitutions. "We will see, in the next year or two," Jorgenson speculated, "a race among chemists to find the compound with 160 K critical temperature. It might be a completely new compound, but at least this work says that it should exist."

Also, according to Jorgenson, these mercury compounds have overturned a certain "folklore in the superconductor community," which held that the T_c of a non-optimized compound could be increased with pressure, but that pressure would have no effect on the T_c of a compound which had already been optimized chemically. The thinking was that pressure was simulating chemical doping by some means, but that once a compound was doped to the optimum T_c, then pressure could not increase it.

However, these mercury compounds show that with pressure, a compound whose T_c has been chemically optimized can increase its T_c even more. Jorgenson pointed out that this "has not been seen in other compounds, and was unexpected. . . . What we now know is that pressure doesn't really simulate doping, that it does more than that, that it modifies the basic electronic structure."

Robert Hazen explained that pressure affects all properties of a material, including the electromagnetic properties. "You can think of pressure as a way of tuning a crystal structure," Hazen said.

Pressure forces atoms closer together, and also changes the chemical bonding by changing the electron interactions among the atoms. Therefore, pressure becomes a tool for exploring how atoms interact, how they bond, and how they behave. High pressure can allow for the probing of new, useful properties in materials, opening the possibility of fabricating new compounds, by chemical means, that have these desired properties under normal conditions.

An additional twist

As an additional twist in this tale, Massimo Marezio and his group at Grenoble reported last December that for a particular sample they had, they saw signs of what could have been superconductivity at about 250 K. Unfortunately, before the researchers were able to confirm their results, the observation generated a lot of publicity, especially in France. "We were caught in the middle," says Marezio.

"What we saw, we saw," Marezio told me. "In our case it was a beautful transition; we published it, and we felt that we were going to reproduce it, but then we had a lot of trouble in doing that." They have not been able to reproduce the sample, so far, even though they can reproduce the exact same preparations. And, while they still have the original sample, the measurements are now regular, in the sense that the compound is a superconductor at 136 K, but no longer shows any of the effects it had at 240 K, which they cannot account for.

Marezio's team does not believe that what they observed was an experimental artifact, but rather that the results seem to be intrinsic to the sample. Marezio thought that it could have been "due to a minority phase which has since then degenerated in the sample." A very small portion of the sample, perhaps less than 1%, could have formed a yet-unknown composition, which was responsible for the unusually high readings and which has since decomposed in the material.

In the late 1980s, during the early stage of the research to achieve high critical temperatures, Marezio said that "people would see something and it would disapear. In most cases it was due to other factors, but sometimes it was true." He continued, "We are still working, and we might come up with something."