Superconductivity Experiments Confirm an Important Mechanism for Increasing the Maximum Critical Temperature in Cuprates

Some cuprate superconductors exhibit high critical temperatures at atmospheric pressure. To understand the underlying processes, researchers recently carried out high-pressure nuclear magnetic resonance experiments on the cuprate $YBa_2Cu_3O_{6+y}$ to determine the charge densities at the Cu and O sites of its CuO_2 plane with high precision. Their results revealed that the more generous the in-plane Cu atoms are in transferring their hole content to the O atoms, the higher the critical temperatures that can be achieved.

By Gianina Buda

This cuprate has been the record-holder since 1993: $HgBa_2CuO_{4+\delta}$ exhibits the highest maximum critical temperature at ambient pressure among all known superconducting compounds, $T_{c,max}$ = 133 K. Other members of this class of materials achieve high T_c values as well. But even though the structures of cuprate compounds share a deceptively simple main feature – they consist of CuO_2 planes interspersed with layers of metal oxides – scientists have struggled to unlock the mechanisms that lead to such high critical temperatures. While the microscopic Bardeen–Cooper–Schrieffer (BCS) theory can explain the behavior of conventional superconductors such as solid Hg, it does not capture the phenomenology of the more "unconventional" superconductors, such as cuprates or iron pnictides, which reach higher T_c values.

But suppose we could understand which material features allow electrons to move freely within them with zero electrical resistance. Then, in principle, we could design the holy grail of the field: a

superconductor that works at room temperature and under atmospheric pressure. Potential technological applications abound: massively reducing losses in global energy systems, improving memory storage devices, designing ultrasensitive sensors, and numerous others.

Pressure and doping effects in cuprates

So how can we get closer to the goal? One way that scientists can vary T_c in a given material is by using chemical doping to modify its electronic structure or other properties: they induce defects in the crystal structure of the compound, which results in a surplus of charge (electron doping) or a deficit of electrons (hole doping) in the unit cell. In the phase diagrams of cuprates (which typically plot T_c against doping), the T_c curve has a dome-like shape, with "optimal" doping corresponding to the top of the dome. Regions to the left and right of this optimal value are called underdoped and overdoped, respectively.

Unfortunately, the value of optimal doping is very similar in all cuprate families (such families comprise materials with the same crystal structure and chemical formula but different concentrations of defects) but yields different family-specific values of $T_{c,max}$ and thus cannot be used to predict this value in a given compound. However, $T_{c,max}$ increases almost linearly with the planar O hole content – which can be manipulated by doping or by applying pressure – and therefore allows such predictions to be made.

The effect of applying pressure has been known for decades: it allows the $T_{c,max}$ specific to a given cuprate family to be surpassed, even in optimally doped cuprates. But how can the effect be explained, and could it hold the key to understanding unconventional superconductivity? In their recent publication in PNAS, "How pressure enhances the critical temperature of superconductivity in $YBa_2Cu_3O_{6+y}$," a group of researchers led by Jürgen Haase came much closer to the answer. Their work is a follow-up on another study, published in 2016 (see here: https://www.nature.com /articles/ncomms11413), in which they had identified the charge distribution in the CuO_2 plane as a formerly unknown parameter that makes it possible to predict $T_{c,max}$. Now, they have identified in great detail how pressure influences the charge distribution in the CuO_2 plane of the cuprate $YBa_2Cu_3O_{6+y}$ (where y = 1 denotes the fully doped compound), or YBCO for short.

From their earlier experiments, Jürgen Haase, Michael Jurkutat, and the other team members knew that a changed charge distribution, or more specifically, electron transfer from O to Cu, increases $T_{c,max}$ for hole-doped cuprates. They also had reason to suspect that pressure – which generally increases T_c in underdoped cuprates – increased hole doping. But how does pressure affect the charge distribution? To find out, the researchers measured the average local charges on the planar Cu and O atoms in novel high-pressure nuclear magnetic resonance (NMR) experiments. Afterward, they examined the relationship between these charges and $T_{c,max}$. As a test object, they chose YBCO microcrystals: here, the difference between the highest T_c achieved by applying pressure and that achieved by doping was markedly high in underdoped samples (e.g. ~18% in $YBa_2Cu_3O_{6.5}$), which suggests that the effect of applying pressure is significant.

Using NMR to quantify the charge content in the CuO_2 plane

Until recently, it was thought that NMR could only be used as a local quantum sensor that provides information about a material's magnetic properties. However, in another earlier work (see here: https://journals.aps.org/prb/abstract/10.1103/PhysRevB.69.094504), Haase and colleagues had extended the realm of what NMR measurements could achieve by developing a new method that was sensitive to the local charge symmetry and determined the values of the local charges on the Cu and O atoms with high precision.

At the beginning of their experiments, the researchers synthesized high-quality YBCO crystals in a

non-reactive crucible and subsequently annealed them in an oxygen atmosphere. This led to fully oxygenated (i.e., fully doped) samples, which were twinned in the CuO_2 plane, or *ab* plane, to account for the slight orthorhombicity of the crystal structure. The idea behind twinning is that the a and b axes alternate periodically, while the c axis remains constant throughout the crystal. This approach allowed the authors to simultaneously measure, with high precision, two crystal orientations with respect to each other. All samples were enriched with ^{17}O, as ^{16}O is NMR inactive due to its matching numbers of protons and neutrons. The researchers obtained the underdoped samples through further annealing and determined the resulting stoichiometries from T_c measurements. Next, they placed the samples in an anvil cell and wrapped radio-frequency microcoils around them. These coils were used to measure the orientation-dependent quadrupole frequencies of the planar Cu and O atoms. Subsequently, they applied pressures of up to 4.4 GPa to the crystals using a hydraulic press. Paraffin oil surrounding the microcrystals ensured that the pressure was applied evenly from all directions.

In NMR experiments, an external magnetic field produces splittings that define the resonance frequencies of the nuclei (^{63}Cu and ^{17}O in this case). The nuclei also interact with the surrounding electric field (an effect known as the quadrupole interaction), which splits the resonance frequencies even further. Measuring these hyperfine frequency differences in all three spatial dimensions allowed the scientists to precisely determine the charge distribution at each atomic nucleus in the CuO_2 plane and, therefore, the hole content of the Cu $3d_{x2-y2}$ and O $2p_\sigma$ bonding orbitals. In the final step, the authors went on to measure the sensitivity of the NMR quadrupole frequencies of the planar Cu and O atoms to pressure.

This complex experimental protocol, however, was not without its fair share of challenges. Occasional disruptions in geometry still occurred, although the pressure applied was high enough to modify the material's electronic properties while not so extreme as to affect the chemical composition or crystal twinning. Another obstacle to overcome was maintaining an adequate signal-to-noise ratio while aligning the crystals with the magnetic field for every pressure point of each sample.

The critical temperature is determined by the energy required for electrons to hop between Cu and O

The experiments showed that the increase in critical temperature with pressure was due to three main factors. First, pressure increased the overall hole doping in the CuO_2 plane compared to chemical doping alone, as expected. Second – and highly relevant for the phenomenon of superconductivity – this increase in hole doping was more favorable for the O than the Cu orbitals and therefore also for T_c, which the researchers knew to be commensurate with the O hole density. Third, the increase in critical temperature was also due to an in-plane charge redistribution. At high levels of doping, and at a given overall hole concentration in the CuO_2 plane, elevated pressure caused the O hole density to rise at the expense of the Cu hole density. That is to say, the orbitals of the two species further hybridized or "mixed" or, as a chemist would put it, the bond between them became more covalent.

The fact that $T_{c,max}$ in cuprates depends on their O hole content may also explain the material-specific dependence of $T_{c,max}$ on pressure. Each class of cuprates (e.g. La-, Bi-, Tl- or Hg-based) has a characteristic charge-transfer gap or bond covalence, which determines the extent of hole sharing between Cu and O and has proven essential in predicting the maximum T_c reached at optimal doping. Theorists tend to think of the Cu–O interaction in terms of this gap, which represents the amount of energy that needs to be overcome by electrons to hop between atoms inside the same unit cell. (This differs from, for example, the Mott gap, which is the energy needed for electrons to hop between unit cells and is a characteristic of the parent – i.e., undoped –

cuprate.) Simply put, the concepts of Cu–O hole sharing, bond covalency, and the charge-transfer gap are different ways of interpreting the mechanism that determines $T_{c,max}$.

Remaining challenges and outlook

Haase's findings have gone a long way toward solving the decades-old mystery of how pressure affects cuprates. However, the findings don't yet provide the whole picture. In YBCO, we now understand why the intrinsic pressure increases the highest temperature at which superconductivity can exist. But we could argue that compounds with different crystal structures and doping levels should respond differently to pressure in terms of their maximum critical temperature. In another class of superconducting cuprates, the LSCO family, for example, T_c increases for all doping levels, which indicates that pressure causes a charge redistribution in the CuO_2 plane. The hole redistribution may be even less straightforward in the Bi-, Tl- and Hg-based cuprates, for which the critical temperature has a nonmonotonic dependence on pressure, such as exhibiting two peaks, which is very different from the dome-like shape.

Also, the influence of the planar O hole content on $T_{c,max}$ and the increase in this temperature in response to pressure compared to what can be achieved by doping alone do not explain why T_c peaks at a specific hole density, or the superconducting dome. The role of the O hole density determines only the *height* of the dome – that is, the value of $T_{c,max}$ – and other cuprate properties, such as the superfluid density at optimal doping and the magnetic properties of undoped or underdoped cuprates.

Nevertheless, the importance of hole-sharing between the Cu $3d_{x^2-y^2}$ and O $2p_{\sigma}$ orbitals in this class of materials and the effect of these microscopic phenomena on $T_{c,max}$ has been clearly demonstrated by this work. While applying pressure in the range of gigapascals isn't feasible for real-world applications, Haase's findings will help theorists and chemists devise other ways to maintain or induce suitable charge distributions in YBCO, as well as in other materials. For example, one avenue might consist in combining other transition metals with chalcogens or pnictides, with which they can form strong covalent bonds. ●

The researchers

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