Cu, Pu and Fe High \( T_c \) Superconductors: All the Same Mechanism

P. Wachter

Abstract

The more than 20 years old Cu high-\( T_c \) superconductors exhibit as undoped parent materials antiferromagnetism. Upon doping the long-range antiferromagnetism disappears and only short-range antiferromagnetic clusters remain which show a spin pseudo-gap. There are no good ideas why long-range antiferromagnetism disappears upon the appearance of superconductivity because antiferromagnetism and superconductivity are compatible.

A breakthrough has come about with the discovery of a plutonium (Pu) containing alloy PuCoGa\(_5\) with a \( T_c \) of 18.5 K. In principle not very exciting, but in the field of actinides \( T_c \)'s are not more than 3 K because of the high mass and corresponding low phonon energies. The compound is a high-\( T_c \) material in the field of actinides. But also this Pu-containing compound is a short-range antiferromagnet with a spin pseudo-gap. A pattern starts to develop! As well in the Cu as in the Pu compounds, some magnetic ions Cu\(^{2+}\) and Pu\(^{3+}\) are replaced upon doping with nonmagnetic Cu\(^{3+}\) or spontaneously with nonmagnetic Pu\(^{2+}\) ions, thus a mixed valence configuration appears with nonmagnetic states (spin holes) in antiferromagnetic clusters.

The newly discovered Fe pnictide superconductors, however, have only one valence, Fe\(^{2+}\) above and below \( T_N \), the Néel temperature of 150 K, as well above and below \( T_c \), as judged by the isomer shift of the Mössbauer effect. However, doping with fluorine, replacing oxygen, not only introduces electrons, but changes locally the crystal field acting on the iron ions. Divalent iron 3d\(^6\) has a high-spin configuration \( t_{2g}^2e_{2g}^2 \) in a magnetic \( \Gamma_5 \) configuration and a nonmagnetic low-spin configuration \( t_{2g}^5 \) in a \( \Gamma_1 \) state. So with the same valence we can have a magnetic and a nonmagnetic configuration, triggered by variation of the local crystal field induced by doping, causing again spin holes.

We show that these spin holes in antiferromagnetic clusters have an attractive interaction and combine to make nonmagnetic bipolarons, which can condense and lead to superconductivity.

Keywords

High \( T_c \) superconductors · Magnetism · Models

1 Introduction

Since the discovery of high-\( T_c \) superconductors by Bednorz and Müller in 1986 [1], for nearly 20 years only copper-containing materials have been known. The \( T_c \)'s vary between about 35 and 164 K for Hg 1223 at 30 GPa [2]. Many theories and models have been proposed as explanation of the mechanism of these cuprates, but there is no general agreement like it was at the times of the BCS theory. There is only agreement that the BCS theory is not able to explain the high \( T_c \)'s of the cuprates. As a consequence there have been no successful proposals that other elements or compounds might also be high-\( T_c \) superconductors.

It thus came to a complete surprise when in 2002 a plutonium alloy has been found, PuCoGa\(_5\), which was superconducting with a \( T_c \) of 18.5 K [3]. Now this by itself is not too exciting. But one has to bring this in connection with superconductivity of other actinides. There are many superconductors in the field of actinides, but their \( T_c \)'s are all less than 3 K, which is plausible since the masses are high, the phonon frequencies are low and thus the \( T_c \)'s are also low. But the enhancement of \( T_c \) between 3 and 18.5 K is more than a factor of 6, about the same enhancement as...
from 23 towards 136 K (without pressure) before and after the cuprates. PuCoGa$_5$ thus is a high-$T_c$ superconductor in the field of actinides. And it is not the only one, replacing Co with rhodium Rh to PuRhGa$_5$ still has a $T_c$ of 8.7 K [4]. Unfortunately, these superconductors are mostly only recognized by physicists in the field of actinides, although on these substances just as many experiments are being performed as on the cuprates and also their single crystals are available.

Again as a surprise, since 2008 Fe pnictides have been realized as high-$T_c$ superconductors, at first as La(O$_{1-x}$F$_x$)$_2$FeP [5], then as La(O$_{1-x}$F$_x$)$_2$FeAs [6] and with highest $T_c$ of 55 K as Sm(O$_{0.8}$F$_{0.2}$)FeAs [7], also in the form of single crystals. It followed the oxygen-free (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ [8] with a highest $T_c$ of 38 K and SrFe$_2$As$_{1.3}$P$_{0.7}$ with 27 K and CaFe$_2$As$_{1.925}$P$_{0.075}$ with 13 K [9].

There are thus three high-$T_c$ superconducting systems and the question is, what is so special about the Cu, Pu and Fe systems and are there similarities? Especially when one looks for theories or models as explanation of the mechanism of superconductivity, we cannot have three different models for the three types of materials, but we must have one unifying model, which works for all.

Now whereas the Cu and Fe systems are highly doped or degenerate semiconductors with lattice defects due to doping, the Pu alloys are undoped metals with a perfect lattice, not even two-dimensional. These different materials then are testing grounds for models or theories, which have to work for all three systems.

2 Comparison of Important Experimental Results

As a first testing ground we want to compare photoemission results on all three systems. Already very early after the discovery of high-$T_c$ cuprates, XPS core level measurements (presented in 1987 at the first International Conference on High $T_c$ Superconductors in Interlaken, Switzerland [10]) were performed on La$_{1.85}$Sr$_{0.15}$CuO$_4$ and reference compounds NaCu$^{3+}$O$_2$, Cu$^{2+}$O and Cu$_2$O. Part of the 3d$^8$, 3d$^9$ and 3d$^{10}$ spectra are shown in Fig. 1. NaCuO$_2$ is a diamagnetic semiconductor [11], CuO is an antiferromagnet and Cu$_2$O is again a diamagnetic semiconductor. The 3d$^n$ lines differ in their half widths, the two diamagnetic compounds having the narrower lines and the antiferromagnetic CuO has nearly twice the line width of the others. It is remarkable and shown at the bottom of the figure by bars, that the energy separation of the three lines with different valences is only about 1 eV, the smallest in the whole periodic system (generally different valences in 3d elements are 3 eV, in rare earths 6 eV, in actinides 3 eV). This in turn means that it costs very little energy to go from one valence to the other. This is one of the essential features in the copper system and it enables thus easily different valences in one and the same compound.

The important aspect is now the spectrum of LASCO, centred at the Cu$^{2+}$ line but with a clearly visible shoulder at the position of the Cu$^{3+}$ line. In fact, on the left side of the figure we repeat the CuO spectrum and add 15% (as given by the chemical formula) of the NaCuO$_2$ line at the right position. The superposition of both lines represents very closely the measured LASCO spectrum. This points to the existence of two valences in LASCO, 85% Cu$^{2+}$ and 15% of Cu$^{3+}$ as the formula demands. The cuprates are thus mixed-valent.

The important point is that our LASCO has no oxygen deficiencies, because we tempered it in streaming oxygen. Only then the shoulder at the position of the Cu$^{3+}$ is measurable. Oxygen and also fluorine are the only two elements which in a compound tear away all possible electrons from a cation in order to fill their p shell completely. The partial substitution of trivalent La by divalent Sr leaves an equivalent amount of oxygen ions in the 2p$^5$ configura-
tion, which compensates by pulling away additional electrons from copper and thus creating Cu$^{3+}$ ions. Inversely, when one has oxygen deficiency in the sample, trivalent Cu is reduced significantly, which is the case e.g. in the classical 123 YBa$_2$Cu$_3$O$_{6+\delta}$, where also XPS measurements have been made. One missing oxygen destroys 2 Cu$^{3+}$ ions. That oxygen really pulls away all possible electrons from a cation such as Cu can be seen clearly by NaCuO$_2$. If one oxygen would remain in the 2p$^5$ configuration, Cu would be divalent and the material would be an antiferromagnetic metal. Instead NaCu$^{3+}$O$_2$ is a diamagnetic insulator [11]. Thus Cu$^{3+}$ 3d$^8$ in octahedral surrounding has no resulting spin. It is thus evident that the hole in the cuprates sits on Cu. The only natural stoichiometric and untwinned compound is single crystalline 124 YBa$_2$Cu$_4$O$_8$, on which UPS or synchrotron photoemission should have been made, but to the knowledge of the author has not been made.

The epic question about where the hole sits in the cuprates, on Cu or on oxygen, is solved with the measurements above. The dispute comes about, because covalency between Cu and O causes a hybridization between their orbits and the hole could also sit on the oxygen, but chemistry and the condition that the p shells of oxygen want to be filled shifts the hole to the larger part of its lifetime towards the Cu$^{3+}$. The holes are least favored on O$^{1-}$ or highly favored on Cu$^{3+}$, as calculations of the Madelung energy show [12]. We will come back to this discussion later on.

Now let us have a look at the photoemission of PuCoGa$_5$, which is shown in Fig. 2 [13]. Here we have a modern UPS measurement on in situ laser ablated single crystals kept at 77 K, with a resolution of 75 meV, ten times better than with XPS on LASCO at 300 K in Fig. 1. The material is not doped but a simple metal with about 1 free electron per formula unit. The direct measurement shows a large and broad (magnetic) peak at about 1 eV below the Fermi energy $E_F$ and a minor narrow (nonmagnetic) peak right below $E_F$. Variation of the excitation energy between HeI and HeII shows that both peaks have f character and thus correspond to Pu with different valences: Pu$^{2+}$ at $E_F$ and Pu$^{3+}$ 1 eV below $E_F$. Again, like in the cuprates, the different valences are only separated by about 1 eV and are indicated in the figure by two bars. The separation of the spectrum in partial density of states reveals also the nonmagnetic 3d$^6$ Co sub-band. Just as in the superconducting cuprates, we have a mixed valence condition of Pu. If we would have had in the XPS measurement on LASCO also a resolution of about 75 meV, we would also have observed a clear separation in two peaks at the different valences instead of only a shoulder.

In Table 1 we show for the various mixed-valence high-$T_c$ superconductors their chemical formulae and the concentrations of the various valences and their magnetic states.

Now let us look at the photoemission of one of the Fe pnictides, undoped LaOFeAs shown in Fig. 3 [14]. This time it is synchrotron light between 15 and 200 eV. Shown in Fig. 3a, just below $E_F$, a narrow peak is growing out with increasing photon energy as typical for a d state of Fe. Between 3 and 6 eV, the states of As and La are centred. In the inset of Fig. 3a we see with 15 eV photon energy that the density of states commences right below $E_F$, which points to the possibility of localized 3d states. In fact, the density of states calculation in Fig. 3b is much broader (about 2 eV) than the measured 3d width (about 05 eV); that is, no sufficient electron correlations are incorporated in the calculation. Again, this points to a (nearly) localized 3d state of iron.

Also, the photoemission has been measured on the 20% F-doped Fe pnictide [14], with practically no difference at
the position of the 3d states and only some changes at about 5 eV, representative of O and As states.

The essential feature of photoemission of the Fe pnictides is that there is no indication of a second valence state with a second 3d peak. Thus the Fe pnictides are not mixed-valent but with only divalent Fe in the 3d⁶ state, as shown in the DOS calculation.

This is confirmed with measurements of the Mössbauer effect as shown in Fig. 4 [15, 16]. On the left-hand side we show undoped LaOFeAs, which is an antiferromagnet...
at about 140 K and the hyperfine splitting into 6 lines is clearly visible at low temperatures. On the right-hand side we show doped and superconducting LaO$_{0.89}$Fe$_{0.11}$As and above and below $T_c$ there is only one isomer line at about 0.5 mm/sec, a value typical for FeS or FeCl$_2$, i.e. divalent Fe. There is no long-range antiferromagnetism anymore and the fast spin fluctuations in the short-range antiferromagnetic clusters cannot be picked up by the isomer shift. A second valence would have resulted in two isomer lines.

Comparing now the three new superconducting systems with Cu, Pu and Fe, there is at first sight no similarity, two are mixed-valent, and one is not.

One of the key parameters in high-$T_c$ superconductors is magnetism. The parent compounds, i.e. the undoped materials, are antiferromagnets. Upon doping into the superconducting composition the long-range antiferromagnetism gets lost. This is best seen in Fig. 5 displaying for the cuprates the phase diagram versus the doping level [17]. With more than 5% doping, the antiferromagnetism disappears and with it the spin gap and only a pseudo-gap with antiferromagnetic clusters or near-ordering remains for the superconducting compositions. It is a fact that antiferromagnetism is not bound to disappear because superconductivity appears. It has been shown already in 1963 [18] that antiferromagnetism and superconductivity are compatible, and in fact there exist quite a few truly antiferromagnetic (low $T_c$) superconductors such e.g. Ce(Co,Rh,Ir)$_3$In$_5$ [19]. It is important to realize that in the cuprates the doping results in a substitution of divalent and magnetic Cu 3$d^9$ with nonmagnetic

| Spin pseudo-gap temperature $T_p$ |
|-----------------------------------|
| Parent compounds antiferromagnets $T_N$ with spin gap |
| La$_2$CuO$_4$, $T_N = 250$ K, YBa$_2$Cu$_3$O$_y$, $T_N = 400$ K |

| Cu Superconductors |
|---------------------|
| Short range antiferromagnetism (spin cluster) with spin pseudo-gap temp. $T_p$ |
| La$_{1.48}$Sr$_{0.52}$CuO$_4$, $T_p = 60$ K ($T_c = 40$ K) |
| YBa$_2$Cu$_3$O$_y$, $T_p = 320$ K ($T_c = 90$ K) |
| YBa$_2$Cu$_3$O$_y$ (124) $T_p = 160$ K ($T_c = 90$ K) |

| Pu Superconductors |
|---------------------|
| Spin clusters with $T_c = 250$ K ($T_p = 18.5$ K) |

Data from inel. neutron scattering, NMR, el. resistivity.

Cu 3$d^8$ or 3$d^{10}$; in short, a substitution with nonmagnetic spin holes.

There has never been a generally accepted explanation why antiferromagnetism disappears when superconductivity appears. But one can take any antiferromagnet and substitute about 10% of its magnetic ions with nonmagnetic ions and the long-range order will get lost. This inversely is also a proof that the doping results in nonmagnetic ions such as Cu 3$d^8$ or 3$d^{10}$.

For the plutonium PuCoGa$_5$ alloy there is no parent material because it is not doped. But the material is nevertheless a short-range antiferromagnet. Susceptibility measurements reveal a Curie Weiss behavior at elevated temperatures with effective moments corresponding to a 5f$^5$ Pu$^{3+}$ configuration but with an extrapolation to a negative paramagnetic Curie temperature of $\Theta_p = -3$ K [3]. Thus there are again antiferromagnetic fluctuations or short-range order such as clusters, etc.

Then what are the two valences observed in the photoemission spectrum? The majority configuration is Pu$^{3+}$5f$^5$ $J = 5/2$, the minority configuration is Pu$^{2+}$5f$^6$ $J = 0$. So again, as in the cuprates, the minority configuration is non-magnetic and is thus preventing the long-range antiferromagnetism. The integrated intensity of the photoemission peaks yields about 10% of Pu$^{2+}$ [13]. As Fig. 5 shows, when antiferromagnetism disappears with its spin gap, then a range of doping with only pseudo-gaps and corresponding temperatures $T_p$ appear. In Table 2 we show the pseudo-gap temperatures for the relevant high-$T_c$ superconductors. Whereas the isotope effect on $T_c$ of the superconductors is very small, it is significant on the pseudo-gap temperature $T_p$. The pseudo-gap temperature can be seen as the Néel temperature of the antiferromagnetic clusters.

But how about the Fe systems which are not mixed-valent and at first sight have no nonmagnetic substitution for the iron? The doping with e.g. fluorine is in the anion lattice, which, however, results in local lattice distortions, involving also nearby irons. We have mentioned already before that the iron in these substances is divalent 3$d^6$. But 3$d^6$ can be
in a high-spin configuration $\Gamma_5$ $t_2^3e^2$ having 5 electrons with spin-up and 1 with spin-down and a total spin $S = 2$. The majority of iron is in this configuration. But $3d^6$ can also be in the low-spin configuration $\Gamma_1$ with $S = 0$, 3 electrons up and 3 electrons down. These are the nonmagnetic states, which we are looking for. The two possible configurations are triggered by the strength of the crystalline field, which in turn depends on the local electric crystal field due to the doping. This is displayed in Fig. 6 where one can see that for small crystal the field $\Gamma_1$ is the ground state and for high crystal field $\Gamma_5$ is the ground state [20].

Now we have the common feature in all three superconducting systems: there are 10 to 20% nonmagnetic states in short-range antiferromagnetic clusters or fluctuations. Now we can show in Fig. 7 a two-dimensional antiferromagnetic cluster having two independent spin holes or nonmagnetic states [21, 22]. In fact we create such a ferromagnetic micro-region around the spin holes (short for nonmagnetic states). These ferromagnetic micro-regions have been named ferrons by Nagaev [23] or magnetic polarons and they have been experimentally observed on the high-$T_c$ 124 superconductors above $T_c$ by magneto-optic depolarization experiments [21]. One single magnetic polaron as in Fig. 7 (upper left) breaks four magnetic bonds to the nearest neighbors; two independent magnetic polarons break eight magnetic bonds. Only seven magnetic bonds are broken for a ferromagnetic (triplet) magnetic bipolaron as in Fig. 7 (upper right), but only six magnetic bonds are broken for a nonmagnetic bipolaron Fig. 7 (lower middle). The net effect is a binding energy due to a gain in magnetic exchange energy of about 0.1 eV per magnetic bond as estimated from the ordering or pseudo-gap temperature $T_p$ of 320 K of e.g. the antiferromagnetic clusters in 123. Thus with a binding energy of about 0.2 eV for a nonmagnetic bipolaron one can support more than even room temperature superconductivity [22].

The gain in magnetic exchange energy upon the formation of a nonmagnetic bipolaron leads to an attractive interaction between the single magnetic polarons and the non-
magnetic bipolarons, which can Bose-condense and lead to superconductivity [24, 25]. It is, however, clear that in this model $T_c$ can never be more than $T_N$ or $T_B$ of the antiferromagnetic clusters.

It is important to realize that this model works for all three high-$T_c$ superconducting systems and the binding energy of the bipolarons is in any case large enough to support the existing $T_c$.

But is there any experimental evidence of Bose condensation of nonmagnetic bipolarons? There are in fact two experiments on stoichiometric and untwinned 124 single crystals, which yield the relevant answers. At first there is an optical reflectivity over nearly 4 decades of photon energy, especially in the far infrared (until 4 meV) and down to 6 K, for light polarization $E_\parallel$ the a- or b-axes of the crystals [21]. From this the optical conductivity for $E_\parallel$ the a-axis (superconducting planes) could be obtained via a Kramers–Kronig relation. For superconductors and $T \to 0$, the optical conductivity goes towards zero for zero photon energy with a delta function at zero photon energy. Above $T_c$, the optical conductivity follows a Drude law and reaches for zero photon energy the dc value of the conductivity. As the temperature decreases to below $T_c$ and to very low values, the optical conductivity becomes continuously reduced. The reduction of the optical conductivity with temperature compared with the conductivity just above $T_c$ (loss of spectral weight) is compensated by an increase of the delta function at zero photon energy (f-sum rule) and it represents the fraction of condensed carriers in the sense of a London two-fluid model. Thus we can derive the thermal population of the superconducting ground state, shown in Fig. 8 as squares. For a Bose condensation of exchange-coupled bipolarons the thermal occupation should follow the empirical two-fluid approximation as $f(T) \propto 1 - (T/T_c)^4$ [26], whereas the BCS theory follows a law $f(T) \propto 1 - (T/T_c)^3$. [27] It is obvious from Fig. 8 that we have a Bose condensation. However, the reflectivity for $E_\parallel$ the b-axis represents simply a Drude term because it has been shown [21] that in the b-direction the chains dominate the plains and thus in the b-direction the behavior is that of a simple metal. It is left to the imagination of the reader to work out how meaningful are experiments on polycrystalline or twinned (123) or other compounds.

In a second relevant experiment we show point contact spectroscopy on 124 single crystals [22], using a golden tip rammed into the crystal, penetrating possible surface contaminations. The results are typical Andreev reflections for the conductance versus voltage. The curve at 4.1 K shows the superconducting gap with a maximum opening of 12 meV, but the shift of the Andreev reflections with temperature follows again the Bose condensation of a two-fluid model and is represented in Fig. 8 by dots.

Thus there can be no doubt that we are dealing with a Bose condensation of nonmagnetic bipolarons as bosons.

3 Comparison of Theories for the Three High-$T_c$ Superconducting Systems

The essence of the paper is to find theories or models, which work for all three superconducting systems, because it appears unreasonable to have for each system a separate theory. Therefore it can be considered a breakthrough when, after more than 20 years of cuprates, finally another high-$T_c$ material has been found with the Pu alloy in 2002. The third system with Fe is a rich group of compounds and it shows the way to future new materials. So far it is essential that a new parent compound is an antiferromagnet, which upon doping loses its long-range magnetic interaction, not because it becomes a superconductor, but because the magnetic ions are so diluted with nonmagnetic ions. It then can become a superconductor.

Of course it is impossible to quote or referee all the existing theoretical proposals. But a new model came up even before the area of high-$T_c$ superconductors began in 1986. This model has been proposed in 1981 by Alexandrov and Ranninger [24, 25]. Here small Fröhlich polarons, i.e. an electron surrounded by a phonon cloud, can bind to become small nonmagnetic bipolarons and Bose-condense to a superconductor (large bipolarons are the Cooper pairs). This model is the father of our proposal of a spin hole in an antiferromagnetic cluster as described above and shown in Fig. 7. We have a small magnetic polaron, called sometimes ferron [23], which has an effective magnetic moment and can pair as a nonmagnetic bipolaron which can Bose-condense and lead to superconductivity. The binding energy of this bipolaron in a magnetic surrounding is much larger than the one of the small Fröhlich polarons of Alexandrov and Ranninger [24, 25].

Shortly after the beginning of the high-$T_c$ area, in 1988 Zhang and Rice [28] developed the so-called t-J model,
where carriers tunnel in an antiferromagnetic lattice. The theory predicted a d-wave symmetry $d_{x^2-y^2}$, as experimentally found in the cuprates. The authors used a single-band effective Hubbard Hamiltonian for their calculations. But a Monte Carlo calculation did not find superconducting correlations [29] and in another paper Su et al. [30] showed that this Hubbard model did not show any long-range pairing and thus no $T_c$ for any non-zero temperature.

However, using instead of the single-band Hubbard Hamiltonian a two-band model, now including also the $3r^2-r^2$ symmetry and permitting both bands coupled by high energy Jahn–Teller phonons, yields more realistic $T_c$ [31] for the cuprates. But the basic idea of K.A. Müller [32] that high energy phonons due to the Jahn–Teller effect in doped Tc for the observed high $T_c$'s does not work in the Pu alloy, which is an undoped metal with about one free electron per formula unit [3], thus screening all electrostatic interactions. Also for the Fe pnictides there is no Jahn–Teller effect, because there is no mixed valence.

As a last model we want to describe the one of Mott [33] which is valid for the cuprates 123 or 124. The model is a bipolaron model with a perfect Cu$^{2+}$ lattice and in some places pairs of oxygen 2p$^5$ ions with spin $\frac{1}{2}$. We have shown already experimentally in the beginning that the hole sits more of its lifetime at the Cu ions thus creating nonmagnetic Cu$^{3+}$ ions instead of the oxygen ions. A 2p$^5$ configuration of oxygen is impossible for chemical reasons when ions of more than one possible valence can exist as neighbors. Since the bipolarons with oxygen are magnetically neutral, the perfect magnetic Cu 3d$^9$ lattice must show antiferromagnetism, which it does not. This model of course does not work for the Pu alloys, but also for the Fe pnictides it is not possible since only oxygen can be a paramagnetic ion, whereas the pnictides like As do not exist as paramagnetic ions.

## 4 Conclusion

In fact it might be said that there are a few polaron and bipolaron models around in which nonmagnetic bipolarons can make a Bose condensation and lead to superconductivity. In fact the first proposal was that of Alexandrov and Ranninger [24, 25], which described this condensation of small Fröhlich-like bipolarons. The binding energy of these bipolarons, however, is much too small to account for the observed high $T_c$'s. The next bipolaron model was that of Mott [33], where the bipolarons are two oxygen 2p$^5$ ions, but no reason is given why these polaron attract each other and become bipolarons. The perfect Cu lattice should lead to antiferromagnetism and it has been shown experimentally that the hole in cuprates sits at the Cu, creating Cu$^{3+}$. Nothing is said about the binding energy of these oxygen bipolarons. Besides, this model can work only for the cuprates.

Our own model of nonmagnetic bipolarons in an antiferromagnetic cluster works for all three high-$T_c$ systems and has a binding energy of the bipolarons which in any case is larger than the existing $T_c$ [21, 22].

Experimentally a Bose condensation of the bipolarons has been verified with the measurement of the thermal occupation of the superconducting ground state.

### References

1. Bednorz, J.G., Müller, K.A.: Z. Phys. B 64, 189 (1986)
2. Chu, C.W., Gao, L., Chen, F., Huang, Z.J., Meng, R.L., Xue, Y.Y.: Nature 365, 323 (1993)
3. Sarrao, J.L., Morales, L.A., Thompson, J.D., Scott, B.L., Stewart, G.R., Wastin, J., Rebizant, J., Bourlet, P., Collineau, E., Lander, G.H.: Nature 420, 292 (2002)
4. Wastin, P., Bourlet, P., Rebizant, J., Collineau, E., Lander, G.: J. Phys. Condens. Matter 15, 2279 (2003)
5. Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H.: J. Am. Chem. Soc. 130, 3296 (2008)
6. Wen, H.H., Mu, G., Fang, L., Yang, H., Zhu, X.: Eur. Phys. Lett. 82, 17009 (2008)
7. Zhigadlo, N.D., Katrych, S., Bukowski, Z., Weyeneth, S., Puźniak, R., Karpinski, J.: J. Phys. Condens. Matter 20, 342202 (2008)
8. Rotter, M., Tegel, M., Johrendt, D.: arXiv:0805.4630 (2008)
9. Shi, H.L., Yang, H.X., Tian, H.F., Lu, J.B., Wang, Z.W., Qin, Y.B., Song, Y.J., Li, J.Q.: J. Phys. Condens. Matter 22, 125702 (2010)
10. Ospelt, M., Henz, J., Kaldis, E., Wachtler, P.: Physica C 153–155, 159 (1988)
11. Hestermann, K., Hoppe, R.: Zeitschrift für anorganische und allgemeine Chemie. Band 367, 261 (1969)
12. Torrance, J.B., Metzger, R.M.: Phys. Rev. Lett. 63, 1515 (1989)
13. Joyce, J.J., Wills, J.M., Durakiewicz, T., Butterfield, M.T., Guziewicz, E., Sarrao, J.L., Morales, L.A., Arko, A.J., Ericson, O.: Phys. Rev. Lett. 91, 176401 (2003)
14. Koitzsch, A., Inosov, D., Fink, J., Knupfer, M., Eschrig, H., Borisenko, S.V., Behr, G., Köhler, A., Werner, J., Bünchler, B., Follath, R., Dürr, H.A.: arXiv:0806.0803 (2008)
15. Klaus, H.H., Luetkens, H., Klingeler, R., Hess, C., Litterst, F.J., Kraken, M., Korshunov, M.M., Eremin, L., Drechsler, S.L., Khasanov, R., Amato, A., Hamann-Borrero, J., Leps, N., Kondrat, A., Behr, G., Werner, J., Bünchler, B.: arXiv:0805.0264 (2008)
16. Kitao, S., Kobayashi, Y., Higashitani, S., Saito, M., Kamihara, Y., Hirano, M., Mitsui, T., Hosono, H., Seto, M.: J. Phys. Soc. Jpn. 77, 103706 (2008)
17. Batlogg, B., Varma, C.M.: Phys. World 33 (2000)
18. Baltensperger, W., Strässler, S.: Phys. kondens. Mater. 1, 20 (1963)
19. Pagliuso, P.G., Petrovic, C., Movshovich, R., Hall, D., Hundley, M.F., Sarrao, J.L., Thompson, J.D.: Z. Fisk. Phys. Rev. B 64, 100503 (2001)
20. Wachtler, P.: Physica C 469, 199 (2009)
21. Wachtler, P., Bucher, B., Pittini, R.: Phys. Rev. B 49, 13164 (1994)
22. Wachtler, P.: Physica C 453, 1 (2007)
23. Nagaev, E.L.: JEPT Lett. 61, 18 (1967)
24. Alexandrov, A., Ranninger, J.: Phys. Rev. B 23, 1796 (1981)
25. Alexandrov, A., Ranninger, J.: Phys. Rev. B 24, 1164 (1981)
26. Tilley, D.R., Tilley, J.: Superfluidity and Superconductivity. Hilger, Bristol (1986)
27. Mühlschlegel, B.: Z. Phys. 155, 313 (1959)
28. Zhang, F.C., Rice, T.M.: Phys. Rev. B 37, 37519 (1988)
29. Morgenstern, I.: Z. Phys. B 70, 291 (1988)
30. Su, G., Suzuki, M.: Phys. Rev. B 58, 117 (1998)
31. Bussmann-Holder, A., Keller, H.: Eur. Phys. J. B 44, 487 (2005)
32. Müller, K.A.: J. Phys. Condens. Matter 19, 251002 (2007)
33. Mott, N.F.: Physica C 205, 191 (1993)