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Similarities between Cu and Pu containing "high T_c" superconductors

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Abstract

PuCoGa$_5$ has with 18.5 K an extremely high T_c for superconductivity compared with other actinide materials having T_cs around 2–3 K. It appears to be a "high T_c superconductor" in the field of actinides. After nearly 20 years of research in high T_c superconductors, only Cu containing materials have T_cs above about 30 K (exception MgB$_2$). BCS theory cannot explain such high transition temperatures, thus other or additional coupling mechanisms like magnetic exchange are necessary. Mixed valence, spin holes in an antiferromagnetic lattice, small energy difference between the various valences and two-dimensionality are common features of Cu and Pu containing superconductors. It can be shown in this paper that the mechanism for superconductivity is the same for Cu and Pu containing materials.
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1. Introduction

The dawn of a new area in superconductivity began in 1986 when Bednorz and Müller [1] and Wu et al. [2] discovered new superconductors of perovskite type with critical temperatures T_c above about 30 K. Since that time only Cu containing materials have T_cs above about 30 K reaching a maximum of 164 K for HgBa$_2$Ca$_2$Cu$_3$O$_8$ [3] at a pressure of 25–30 GPa. One exception is MgB$_2$ with a T_c of 40 K, which has an unusual strong nesting of its Fermi surface [4] and multiple gaps. In our opinion, enough attention has not been paid to the fact that after nearly 20 years of international research only Cu seems to be able to produce high T_c superconductivity. The question must be asked, what is so special about copper?

The actinides and their alloys or compounds are usually no interesting candidates for superconductivity. For the lighter actinides one has 5f bands, so 5f electrons at the Fermi level E_F are directly involved in the conduction mechanism. Since in the actinides the mass is very large, the typical phonon frequencies are low and thus also T_c. Therefore, the actinides have in general T_cs in the order of some degrees. It thus came as a surprise that recently with PuCoGa$_5$ [5] a T_c of 18.5 K has been discovered and it has soon been recognized that this material is a representative of a "high T_c superconductor" in the field of actinides. Even more recently also PuRhGa$_5$ has been found with a T_c of 8.7 K [6]. Now Pu and Am are elements where the 5f electrons are on the verge of localization, in the 7 crystallographic phases of elemental Pu from the α to the δ phase such a transition from localized to delocalized seems to be verified. But none of the phases of elemental Pu are superconducting, just as copper itself is not a superconductor. Am, however, is superconducting. Then there is more to it.

It is then the purpose of this paper to find out similarities between the physical properties of Cu and Pu containing compounds and alloys to get a consistent view of what is essential to make high T_c superconductors. In this task we also have to reconsider some models for Cu high T_c superconductors which were left in question and which

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now gain confidence, when the same mechanism turns out to be valid also in the new Pu "high T_c" actinide superconductors.

2. Experiments and models, a critical evaluation of Cu high T_cs

One of the earliest experiments, not directly related to the measurements of T_c, magnetic susceptibility, specific heat or other classical experiments typical for superconductivity, was XPS (resolution 0.8 eV) core level photoemission on Cu compounds having various Cu valences, including the superconductor $La_{2-x}Sr_xCuO_4$ [7–9]. In Fig. 1, we show combined results of Refs. [8,9] of spin–orbit split $2p_{1/2}$ and $2p_{3/2}$ states with satellites. The curves represent final state spectra where the core hole created by the photoemission process is screened either by oxygen p electrons (ligand L) or by other d electrons. The naming of the peaks, however, refers to the initial state. The peaks of lowest binding energy are plotted for $NaCu^{3+}O_2^{2-}$, $Cu^{2+}O^{2-}$, $La_{1.85}Sr_{0.15}Cu_{0.15}^{3+}Cu_{0.85}^{2+}O_4^{2-}$ and $Cu_2^{1+}O^{2-}$. The formulae represent the fulfillment of the octet rule and we assume neither oxygen vacancies nor O^{1-} ions. To avoid oxygen vacancies, the samples have been sintered in streaming oxygen or in case of CuO have been cold pressed, because this material loses oxygen upon heating. One oxygen vacancy destroys $2Cu^{3+}$ ions, in the Cu^{2+} matrix. Thus, if one wants to see the fingerprint of Cu^{3+} ions, it is essential to have no oxygen vacancies. Now Cu^{1+} is in a $3d^{10}$ configuration and Cu^{3+} is in a $3d^8$ configuration and both have no magnetic moment in the perovskite structure and the compounds Cu_2O and $NaCuO_2$ indeed are diamagnetic, showing also that one has no O^{1-} ions, because the $2p^5$ configuration is paramagnetic.

The two diamagnetic compounds $NaCuO_2$ and Cu_2O shown in Fig. 1 have narrow line widths of 1.8 eV and 1.4 eV, respectively, appreciably more than the sp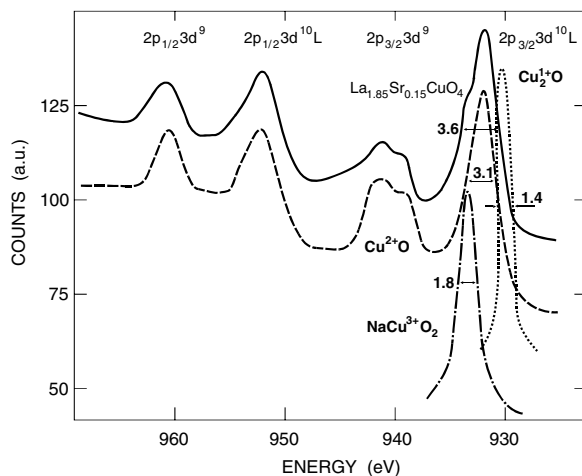ectral resolution. However, CuO and the not shown parent substance La_2CuO_4 of the superconductor have a large line width of 3.1 eV, but appreciably less than in Ref. [8], due to our special oxygen treatment. Both compounds are antiferromagnets with 240 K [10] and 250 K [11], respectively. Magnetic exchange energy is probably the reason for this larger line width compared with the diamagnetic compounds.

An even more important point is the position in energy of the lowest energy peaks of the core electron spectra for the various valences. As can be seen from Fig. 1, the energy difference for Cu^{1+}, Cu^{2+} and Cu^{3+} is only about 1.0–1.5 eV [9], in agreement with Ref. [8]. This energy difference for Cu^{n+} is the smallest in the whole periodic system and is *one of the specialities of Cu*. Typically, for 3d elements this difference amounts to about 3 eV, for the rare earths to about 6 eV and for the actinides to about 4 eV. A small energy difference is essential in a mixed valence situation, so that oxygen can tear away some electrons from Cu^{2+} to fill its p shell to the $2p^6$ state. An experimental proof is the diamagnetism of insulating $NaCu^{3+}O_2^{2-}$. The alternative situation would be $NaCu^{1+}O_2^{1-}$, which would be a paramagnetic insulator or $NaCu^{2+}O_2^{1-}$, which would be a paramagnetic metal.

If we now look at the photoemission spectrum of the superconducting composition $La_{1.85}Sr_{0.15}CuO_4$ in Fig. 1, we can clearly discern a shoulder, exactly at the position in energy where Cu^{3+} is observed in $NaCuO_2$. In Fig. 2, we normalize the various peak heights and add 15% of Cu^{3+} with the right energy and width to the Cu^{2+} peak. The result reproduces the experimental curve very well and thus is a proof of the mixed valence situation in the superconductor. We want to remark that this observation is only possible when no oxygen vacancies are present, which we avoided with the special oxygen treatment. Nevertheless, this material is superconducting with a T_c

Fig. 1. 2p core level spectra of $La_{1.85}Sr_{0.15}CuO_4$, CuO, Cu_2O and $NaCuO_2$. Spectral resolution, 0.8 eV [8,9].

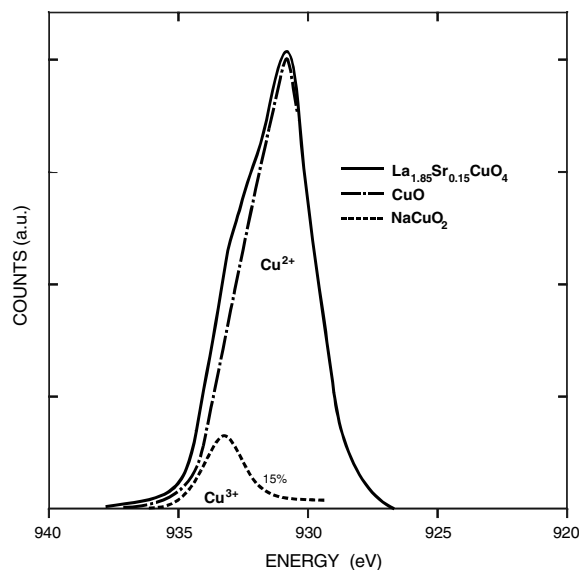
Fig. 2. Decomposition of the $2p_{3/2}3d^{10}L$ state of $La_{1.85}Sr_{0.15}O_4$ into di- and trivalent contributions, taken from CuO and $NaCuO_2$ spectra.

of 34 K [9]. It is not the highest T_c in the series, which amounts to about 40 K, although it has the composition reported for the highest T_c, namely 15% Sr. However, materials prepared in the general scheme have oxygen vacancies, which destroy several Cu^{3+}. So the maximum T_c of nearly 40 K is positioned at about 10% Sr in the absence of oxygen vacancies. A similar photoemission experiment is exactly giving an evidence of this [7]. The authors find a small shift of the Cu $2p_{3/2}$ lines for superconducting compositions towards the trivalent position (and an increase in its half width), but they also find a considerable amount of oxygen defects. *Thus a mixed valence situation is essential for Cu high T_c superconductivity*. A support for this condition is obtained also from $La_2CuO_{4.6}$ [12] where excess oxygen pulls away additional electrons from Cu^{2+}, creating thus again Cu^{3+} ions and the mixed valence condition, resulting in ("filamentary", sic) superconductivity at about 40 K.

Also the other standard Cu high T_c superconductors are of mixed Cu valence, as can be seen from the octet rule: $YBa_2Cu_3O_7(123) \equiv Y^{3+}Ba_2^{2+}Cu_1^{3+}Cu_2^{2+}O_7^{2-}$ (overdoped, twinned SC, $T_c \approx 90$ K, 33% Cu^{3+}), or $YBa_2Cu_4O_8$-(124) $\equiv Y^{3+}Ba_2^{2+}Cu_1^{3+}Cu_3^{2+}O_8^{2-}$ (naturally underdoped, untwinned, stoichiometric SC, $T_c \approx 81$ K, 25% Cu^{3+} [13]). Other related Cu perovskites are $Pr^{4+}Ba_2^{2+}Cu_3^{2+}O_7^{2-}$ (insulator) and $Y_{0.75}^{3+}Pr_{0.5}^{3.5+}Ba_2^{2+}Cu_3^{2+}O_7^{2-}$ (mixed valent Pr, metal).

Some authors consider this mixed valence arguments only as a formal valence since Cu d electrons and oxygen p electrons hybridize, giving rise to some covalency. But no material is 100% ionic, even LiF has only 89% ionicity [14]. In this connection, it is essential that oxygen has the strongest affinity (compared with S or Se) for the last electron in its p-shell and the energy difference between Cu^{2+} and Cu^{3+} is only about 1 eV, the smallest value known so far. Note that for all copper oxides, including La_2CuO_4 and the Cu containing superconductors, the holes are least favoured on O^{1-} or highly favoured on Cu^{3+}, as calculations of the Madelung energy show [15].

But one oxygen vacancy destroys two Cu^{3+} ions, so in general the typical 123 SC with oxygen vacancies has reduced the Cu^{3+} content to non-detectability. This is not so in 124 which is stoichiometric by nature [13].

Generally speaking the Cu high T_c superconductors are p-type conducting due to the introduction of Cu^{3+} in the Cu^{2+} matrix. However, the SC compound $Nd_{2-x}Ce_xCuO_4$, by using the octet rule, must be written $Nd_{2-x}^{3+}Ce_x^{4+}$-$Cu_{1-x}^{2+}Cu_x^{1+}O_4^{2-}$ and is n-type conducting [16] and contains the nonmagnetic $Cu^{1+}(3d^{10})$. The highest T_c is 24 K and is achieved with $x = 0.15$ Ce. *Thus, n- or p-type conductivity is not of great relevance for high T_c superconductivity*.

There are some claims that in 123 SC the mixed valence is achieved by Cu^{1+}, instead of Cu^{3+} [17]. Whereas in this and other papers by the same authors, in XPS on the Cu $(2p_{3/2})$ line no indication of mixed valence is observed, in agreement with Ref. [8], a Cu (L_3VV) Auger spectrum seems to indicate the presence of Cu^{1+}. However, no statement is made as to the degree of oxidation. The difference

in position between the Cu^{2+} and Cu^{1+} lines is with about 5 eV much too large. In Refs. [7–9] this difference has been measured to be only about 1 eV. So the Auger spectrum is probably caused by oxygen non-stoichiometry or surface effects and cannot be considered as proof for Cu^{1+}. But in any case, *for interpretation of HTSC a mixed valence condition is essential and the valences other than Cu^{2+} must be in a nonmagnetic state, which is the case as well for Cu^{3+} as for Cu^{1+}*.

The majority Cu^{2+} ions are in the $3d^9$ configuration and suffer a cooperative Jahn–Teller distortion with an elongated c/a ratio of the oxygen octahedrons. Cu^{3+} $3d^8$ and Cu^{1+} $3d^{10}$ are not Jahn–Teller ions and thus the oxygen octahedrons are not elongated. But the ionic radius of $Cu^{3+} < Cu^{2+} < Cu^{1+}$ [14], thus there is appreciable lattice distortion around the minority ions in the Cu–O plane. Electrons or holes trapped at the minority Cu ions thus form dielectric polarons and they are mobile in the lattice by exchanging charge with the majority Cu^{2+} ions. Eventually two such polarons become neighbours and they bind together as bipolarons. As has been shown by Chakraverti and Ranninger [18], such bipolarons in a concentration of about 10% of the Cu^{2+} ions can make a Bose condensation and lead to superconductivity.

Can such nonmagnetic bipolarons in a *nonmagnetic matrix* by themselves result in superconductivity? Yes they can and it has been shown in the case of $BaBiO_3$ [19], which can be written also as $Ba_2Bi^{3+}Bi^{5+}O_6$. This compound can be regarded as a lattice ordering of bipolarons, stabilized by the lattice distortion of the oxygen octahedrons. Disturbing the perfect unit cell doubling by doping with potassium as $Ba_{1-x}K_xBiO_3$, the bipolarons become mobile and one obtains with $x = 0.4$ a T_c of about 30 K. The bipolaron binding energy is of course much larger than the phonon induced binding energy of two electrons in a BCS model; nevertheless, these materials are no high T_c superconductors, as also Alexandrov et al. [20] showed theoretically.

Another example is Ti_4O_7, where the bipolaronic order can be seen by doubling the unit cell to $Ti_8O_{14} = Ti_4^{3+}Ti_4^{4+}O_{14}^{2-}$, an equal mixture of Ti^{3+} $3d^1$ and Ti^{4+} $3d^0$ ions. Contrary to the first expectations, this material is non-metallic and diamagnetic at low temperatures, the spins of Ti^{3+} compensate perfectly [21]. Doping this compound can make the bipolarons mobile, but the material at the same time becomes magnetic and not superconducting. It is also quite clear that in Ti_4O_7 the oxygen ions have been able to tear away a 4th electron from 50% of the Ti ions to fill their p shells completely. The possible existence of O^{1-} ions and the corresponding excess of Ti^{3+} ions would have made the material paramagnetic, which is not the case.

It has already been mentioned that the actinide compound $PuCoGa_5$ as an intermetallic alloy (with much more electrons per formula unit than the doped Cu compounds [5]) cannot support dielectric polarons or bipolarons due to charge screening. *In other words, dielectric bipolarons alone cannot provoke high T_c superconductivity appreciably*

above 30 K, a unifying proposal for the Cu and Pu superconductors must be sought in another mechanism.

A common feature of Cu containing SC is that the parent compounds are antiferromagnets, such as La_2CuO_4 with $T_N = 250$ K [11] and $YBa_2Cu_3O_6$ with $T_N = 400$ K [22]. In each case the long-range antiferromagnetism, as determined by elastic neutron scattering, is destroyed in the SC compositions. The result is either a spin glass or a frustrated antiferromagnet. In the copper compounds in Cu^{2+}, the higher lying $e_g \, |x^2 - y^2\rangle$ state is occupied with only one electron and is thus in a spin 1/2 state.

The introduction of 10–15% spin holes in the form of nonmagnetic Cu^{3+} or Cu^{1+} destroys the long-range antiferromagnetism in Cu SC, and gives rise to a spin glass or cluster region, as it would do so also in any other non SC antiferromagnet. But whereas a classical long-range antiferromagnet has a spin gap, these short-range antiferromagnetic fluctuations or clusters have only a *pseudogap*, which does not extend over the whole Brillouin zone. The minimum concentration of spin holes to destroy long-range antiferromagnetism is given by the percolation limit, which is smaller in 2 ($\approx$12%) dimensions than in 3 ($\approx$15%). *This seems to be the main reason why two-dimensionality helps in HTSC. But it is not essential.* A three-dimensional cubic copper oxide HTSC is Tl–Tb–Sr–Ca–Ba–Cu–O–F in ceramic form with a T_c of 117 K [23].

A spin hole such as Cu^{3+} or Cu^{1+} in an antiferromagnetic two-dimensional cluster acts as a small ferromagnetic region, termed a magnetic polaron by Nagaev [24] or later even a ferron [25]. But also when the hole sits on a $2p^5 \, O^{1-}$ ion, its spin of 1/2 can polarize some neighbouring Cu^{2+} ions antiparallel to itself and create a ferromagnetic micro-region [26].

Then there are basically two proposals of such ferrons. The models of de Jongh [27,28] and Wachter and Degiorgi [10] assume antiferromagnetic Cu^{2+} clusters with some nonmagnetic Cu^{3+} or Cu^{1+} ions dispersed in them and only O^{2-} ions. This proposal is displayed in Fig. 3a. Mott [29–31] assumes an undisturbed Cu^{2+} spin 1/2 lattice with spins of 1/2 sitting at some O^{1-} ions, causing ferrons. This model is displayed in Fig. 4a, region A. In Mott's model the copper spins form no antiferromagnetic clusters and there is no ordering temperature. Away from the O^{1-} ions, the copper spins $3d^9$ "resonate". The problem boils down again to the question where sits the hole? In the copper or in the oxygen ions! Above we have given reasonable arguments that the hole rather sits in the copper lattice.

When there is no long-range antiferromagnetism, spin pseudo-gaps must nevertheless exist in the antiferromagnetic clusters. A transition across this pseudo-gap is electric dipole forbidden because it is a spin flip transition. But NMR and related techniques [32], like spin–lattice-relaxation, electrical conductivity [33], Hall effect [34] and inelastic neutron scattering [22] confirm the spin pseudo-gaps, which exist only in the antiferromagnetic clusters.

Experimentally, we should concentrate on untwinned, underdoped and naturally stoichiometric $YBa_2Cu_4O_8$-

a

MAGNETIC POLARON

b

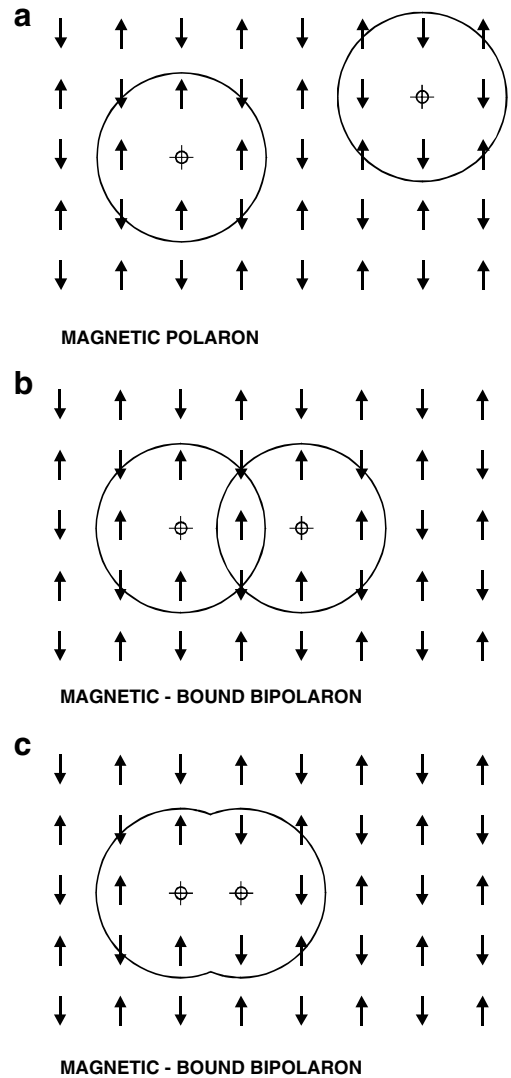**MAGNETIC - BOUND BIPOLARON**

c

MAGNETIC - BOUND BIPOLARON

Fig. 3. (a) Two separated spin holes ($3d^8$) in an antiferromagnetic cluster. (b) Two spin holes with attractive interaction forming a triplet bipolaron. (c) Two spin holes with attractive interaction forming a nonmagnetic singlet bipolaron, after [10,27,28].

(124) single crystals, because only measurements on these compounds are comparable. Polycrystalline 124 is grown under 300 bar oxygen pressure and has a T_c of 81 K [13]. Single crystals of 124 are grown at a higher temperature than polycrystalline material and thus need 600 bar of oxygen pressure. The growth in Al_2O_3 crucibles contaminated the crystals with traces of Al, which reduce T_c to 72 K. A growth in Y_2O_3 crucibles retains a T_c of 81 K. The single crystals described in this work had a T_c of 72 K.

Can one observe the existence of ferrons? In the model of de Jongh [27,28] and Wachter and Degiorgi [10], they can only exist in an antiferromagnetic surrounding, similar to that shown in Fig. 3a, i.e. below the ordering temperature of the antiferromagnetic clusters. This in fact is the pseudo-gap temperature T_p. Here Wachter et al. [33] made a critical experiment. Linearly polarized light is reflected from an untwinned 124 single crystal and passed through a crossed
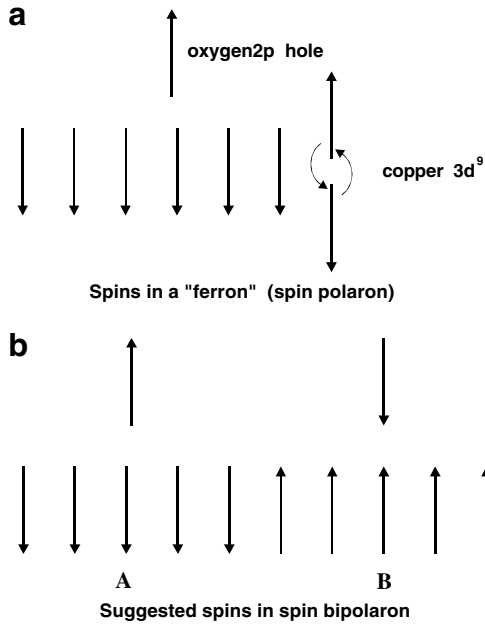
Fig. 4. (a) Oxygen $2p^5$ holes with spin 1/2 polarizing close by Cu $3d^9$ spin 1/2 ions (region A). Outside region A the Cu $3d^9$ are "resonating". (b) Two oxygen $2p^5$ holes with attractive interaction form nonmagnetic singlet bipolarons (region AB). Outside region AB, the Cu $3d^9$ are "resonating" [29–31].

Fig. 5. Temperature dependence of the depolarization of $YBa_2Cu_4O_8$ single crystals due to ferrons or magnetic polarons [33].

analyzer. The incident polarization is arranged relatively to the crystal axes a and b so as to obtain maximum extinction. At 300 K an extinction to 2% is obtained as a result of an ellipticity due to the different crystallographic axes a and b. But below about 200 K ($T_c = 72$ K), a depolarization sets in as shown in Fig. 5. A Faraday modulator cannot reduce this depolarization at any angle. A simple antiferromagnetic cluster cannot depolarize the reflected light because there is no net magnetization. However, individual ferromagnetic micro-regions (magnetic polarons, ferrons, ferromagnetic bipolarons (triplet state)) will cause local Kerr rotations, right and left handed with respect to the incident light polarization. As a consequence the analyzer cannot extinguish the reflected light to the same degree and a depolarization sets in between 150 K and 200 K, i.e. far above T_c. The opening of the pseudo-gap follows a spin correlation function (see Fig. 5) and we find the ordering temperature of the antiferromagnetic clusters near 160 K or 14 meV. This temperature T_p is consistent with other types of measurements [32–34] on 124. In LaSrCuO this temperature is about 60 K ($T_c \approx 40$ K) [35] and in 123 it is 320 K [22] ($T_c \approx 90$ K). In Mott's model there is no specific temperature when magnetic polarons or ferrons should appear, certainly far above T_c.

There is a mutual magnetic attraction between the magnetic polarons or ferrons to form nonmagnetic bipolarons (Figs. 3c and 4b), *which then can make a Bose condensation at T_c and cause superconductivity*, as predicted by Alexandrov et al. [20] and Mott [29–31]. One single magnetic polaron as in Fig. 3a breaks four magnetic bonds to the
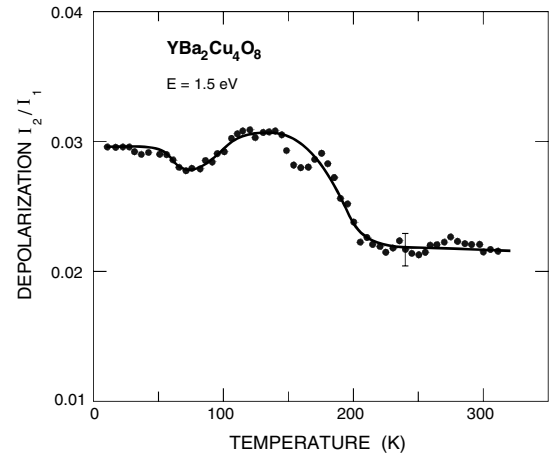
nearest neighbours; two independent magnetic polarons break eight magnetic bonds. Only seven magnetic bonds are broken for a ferromagnetic (triplet) magnetic bipolaron as in Fig. 3b but only six magnetic bonds are broken for a nonmagnetic bipolaron (Fig. 3c). The net effect is a binding energy due to 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 the antiferromagnetic clusters in 123. Thus with a binding energy of about 0.2 eV for a nonmagnetic bipolaron in 123, one can even support room temperature superconductivity. In Mott's model, two oxygen holes with spin 1/2 polarize a few neighbouring Cu ions antiparallel to each other as in Fig. 4b. In the region AB, the normal antiferromagnetic forces give rise to binding of a singlet bipolaron. In both models, of course, one must realize that the magnetically coupled singlet bipolarons are also pairs of two equal electric charges, namely holes in general for the Cu SC, which due to their lattice distortion interact also with phonons, just as in the BCS model. Thus there is also an, albeit small, ^{18}O–^{16}O or ^{65}Cu–^{63}Cu isotope effect on T_c, in 124 0.4 K, and a much larger isotope effect on T_p, in 124 50 K, for the oxygen substitution and 25 K for the Cu substitution [35]. This appears reasonable, since in the model of Fig. 3 no oxygen ions are involved and the isotope effect on T_c comes only via the small phonon contribution. However, T_p is caused by an indirect antiferromagnetic superexchange Cu^{2+}–O–Cu^{2+}, involving directly oxygen and Cu ions and their coupling to the lattice via spin–lattice relaxation. On the other hand in Mott's model, represented in Fig. 4 with O^{1-} bipolarons, an O^{16}–O^{18} isotope effect should be large on T_c, which is not the case. Here, we just wanted to show that phonon coupling alone and also dielectric Jahn-Teller bipolarons alone cannot account for T_cs larger than about 30–40 K.

There is a basic difference between the models shown in Figs. 3 and 4. In Fig. 3, a nonmagnetic Cu^{3+} $3d^8$ spin hole is shown which creates the magnetic polaron or ferron

around itself, two spin holes together form a nonmagnetic bipolaron, but a triplet bipolaron as shown in Fig. 3b has a smaller binding energy than the nonmagnetic (singlet) bipolaron. In Fig. 4 the oxygen O^{1-} has a spin and forms a magnetic polaron, two such polarons can be in a nonmagnetic singlet or in a magnetic triplet state with the triplet having a smaller binding energy. In any case the nonmagnetic bipolarons can make a Bose condensation to superconductivity.

On observation of Fig. 5 it is seen that the formation of nonmagnetic bipolarons occurs above T_c at about 110 K, where the optical depolarization becomes reduced. Below about 72 K, however, the depolarization increases again, but this time it is the effect of an enhanced ellipticity due to different contraction of the a and b-axes in the superconducting state.

An interesting observation [33] in 124 is that the temperature dependence for the resistivity for current parallel to the chain b-axis reveals a simple Bloch–Grüneisen relation as expected for a normal metal. But for current parallel to the a-axis, i.e. in the Cu–O plane, a kink is observed near 160 K with a reduced slope above 160 K. The resistivity above T_c is in no case linear, as has been claimed (e.g. [29]) several times on twinned, non-stoichiometric and polycrystalline 123 samples. We propose that for temperatures below the pseudo-gap of 160 K the spins are frozen and the spin pseudo-gap opens, thus the spin scattering channel closes and only the phonon scattering remains; hence the resistivity decreases faster with decreasing temperature. Mott [36] proposes that for temperatures above the pseudo-gap temperature of 160 K (without using this terminology), triplet bipolarons can be thermally excited, whereas below this temperature only singlet bipolarons can exist. Mott estimates that above 160 K, 3/4 of the carriers will be triplet bipolarons. Now this is certainly not substantiated by the depolarization measurements in Fig. 5, which show that above the pseudo-gap temperature ferrons or triplet bipolarons, if at all, have a very low concentration. Also singlet bipolarons do not come into existence below 160 K but only ferrons in the antiferromagnetic clusters, with singlet bipolarons coming into play only near 110 K. In Mott's model (Fig. 4) an ordering temperature T_p of antiferromagnetic clusters does not exist.

So there is no doubt that a spin pseudo-gap T_p of 160 K or 14 meV occurs in 124 in the antiferromagnetic clusters, ferrons exist and by mutual attraction form singlet bipolarons already above T_c and Bose condense at T_c.

But how about a charge gap in these superconductors? Superconductors as a result of a Bose condensation are gapless, because bosons give a specific heat varying as T^3 instead of $\exp(-\Delta/k_B T)$ [29,37]. Evidence for this is coming from a relatively high γ-value of the specific heat of about 2 mJ/moleK^2 in the superconducting state [38]. Generally speaking, charge gaps in superconductors can be measured by optical means or by tunnelling and in 124 untwinned single crystals both techniques have been applied. Here,

we have to keep in mind that optical measurements are high frequency results ($\approx 10^{12}$ Hz), whereas tunnelling is essentially dc. This caveat may be of relevance in a resonating valence bond (RVB) model.

The polarized (parallel to the a- and b-axes) optical reflectivity on 124 has been measured [33] between 4 meV and 12 eV photon energy (unpolarized down to 1 meV) for various temperatures above 6 K and been analyzed with Kramers–Kronig techniques for the optical conductivity. The reflectivity at 6 K (i.e. 1/12 of T_c) in the far infrared, polarized parallel to the b (chain axis), is typical for a metal. But polarized parallel to the a-axis (i.e. in the Cu–O plane), the reflectivity shows a lot of structure. Optical conductivity reveals a lowest energy peak at 28 meV with no clear-cut edge towards the lowest energies below which the conductivity becomes zero until the δ-function at zero energy. This is in contrast to the optical conductivity of, e.g. Rb_3C_{60} with a T_c of only 29 K, measured with the same equipment and the same method, where one observes an absolute zero line at 6 K [39]. In 124 there seem to be still some uncondensed carriers around, either fermions, unpaired magnetic polarons or ferromagnetic bipolarons as depicted in Fig. 3b. Whereas in Rb_3C_{60} one certainly has s-wave pairing [39], this cannot be the case in 124. The experiment is only compatible with a gap as in d-wave pairing where the gap becomes zero at some k vector. Its maximal opening can be estimated to be about 10 meV [33]. Unfortunately, there is no angular resolved photoemission (ARPES) on 124 to determine at which k vector the gap becomes zero.

Classical tunnelling experiments are not known on 124 but point contact spectroscopy has been performed [40]. A carefully etched gold electrode has been rammed into the surface of a 124 untwinned single crystal, penetrating possible surface contaminations. The curves represented in Fig. 6 show typical Andreev reflections for the conductance versus voltage. The curve at 4.1 K (1/17 of T_c) still does not show a flat zero bottom line as would be typical for classical s-wave superconductors (see the inset of Fig. 6). It must be concluded that there is still some density of states in the gap with uncondensed carriers. This conclusion is the same as obtained from the optical spectra on 124 (above).

There may be questions about a "Coulomb staircase" in these types of measurements, as has been discussed with scanning tunnelling spectroscopy with an STM on $HgBa_2Ca_2Cu_3O_{8+\delta}$ single crystals where insulating surface islands get tunnelled [41] and can result in the observed structures. However, on 124 we have observed a strong and typical temperature dependence of a gap and related structures (dashed lines), going towards zero at T_c. Insulating surface islands should not exist in stoichiometric 124 and if so tunnelling through them would not be temperature dependent.

The maximum opening of the gap is about 12 meV. Practically the same as that obtained from the optical measurements. Thus $2\Delta/k_B T_c$ (72 K) = 3.5 seemingly as in the weak coupling BCS limit.

We can calculate the thermal occupation of the super-fluid ground state. From the optical data, we can use the f-sum rule to determine the superconducting fraction of the free carriers. We show this in Fig. 7 (squares) where the thermal occupation has been normalized to the value at 6 K [33]. For a Bose condensation of exchange coupled bipolarons, the thermal occupation should follow the empirical two-fluid approximation $n_s \propto 1 - (T/T_c)^4$ [37]. In the BCS limit, we would obtain an exponent of 3 [42].
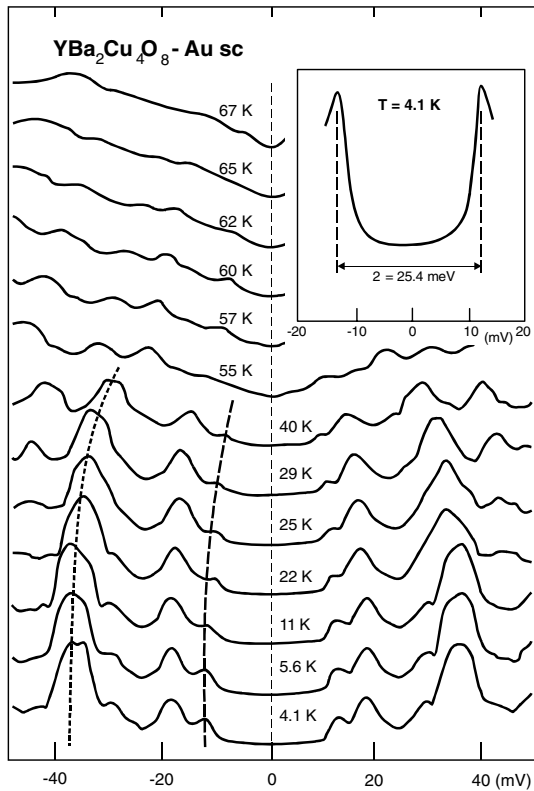

Fig. 6. Point contact spectroscopy on $YBa_2Cu_4O_8$ single crystals. The lines through the Andreev reflections serve as guide to the eyes. The inset shows the enlarged center region at 4.1 K [40].
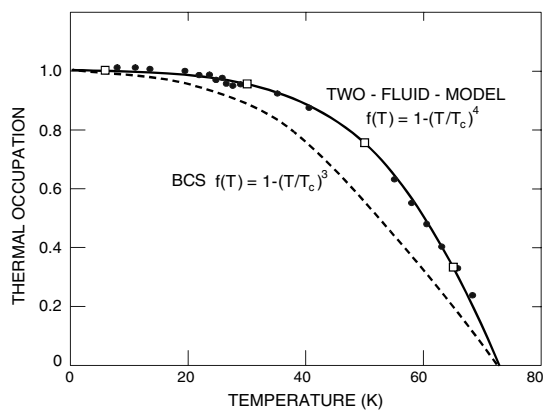

Fig. 7. Thermal occupation of the superconducting ground state as deduced from f-sum calculations (squares) or the temperature dependence of the Andreev reflections (points) in the two-fluid model. For comparison also the BCS model is shown [33,40].

Both curves are shown in Fig. 7 and the optical results (squares) clearly point to a Bose condensation. But we can also plot the thermal shift of the tunnelling gap or the wings from Fig. 6 into the same diagram, normalized at 4.1 K (dots). Also these data follow exactly the Bose condensation model.

So it seems to be established that in 124 one has a gap with nodes as in d-wave pairing with maximal opening of 10–12 meV and a Bose condensation of nonmagnetic bipolarons. By definition, the Fermi level is where the gap becomes zero, granting also that the specific heat follows a T^3 law.

3. Experiments and models for Pu high T_cs

It is the purpose of this paper to compare the physical properties of the recently discovered superconducting alloys $PuCoGa_5$ [5] and $PuRhGa_5$ [6] with T_c of 18.5 K and 8.7 K, respectively, with the well-known Cu high T_c superconductors. The Pu alloys have been called "high T_c superconductors" in the field of actinides. Naturally much more information is available on $PuCoGa_5$, so we will concentrate on this material.

For this and related alloys single crystals are available and problems like stoichiometry as in the Cu compounds are less important. Technically, a self-heating and aging effect due to the radioactive decay is present and low temperature measurements must be corrected for this. The materials are tetragonal with a c/a ratio near 1.6 [43]. A tetragonal crystal structure goes in the direction of two-dimensionality, but of course, not as far as two-dimensional Cu–O planes in the perovskites. Nevertheless, a band structure calculation of $PuCoGa_5$ [44] shows *a two-dimensional Fermi surface* comprising corrugated cylindrical sheets along the c-axis.

Since the material exhibits magnetism, the role of Co or Rh must be cleared. But as structural data [43] show Co and Rh in mixed crystals, $PuCo_xRh_{1-x}Ga_5$ merely act as neutral spacers with T_c and lattice constants varying nearly linearly with x. Thus, Co and Rh must be in the nonmagnetic trivalent $3d^6$ and $4d^6$ configuration, respectively, with t_{2g} bands filled completely.

Since trivalent Pu $5f^5$ is in a magnetic $J = 5/2$ state, the material could exhibit an ordered magnetic state. But since it is superconducting, ferromagnetism is unlikely, but anti-ferromagnetism is an option. One must recall that since the famous theoretical paper by Baltensperger and Strässler [45] antiferromagnetism and superconductivity are no antagonists. And in fact $Ce(Rh,Ir)In_5$ [46] and others are simultaneously antiferromagnets and low T_c superconductors. So if $PuCoGa_5$ wants to be an antiferromagnet, it does not have to loose this property to become a superconductor. *But there is no long-range antiferromagnetic order* [5,47].

Similar as for the Cu HTSC one may look for an anti-ferromagnetic parent material, but there seems to be none. Some authors think δ-Pu may be it, but it is no antiferro-magnet and similarities are only that the 5f states are on

the verge of localization [48] in both materials. Others think that Pu $5f^5$ is the hole-analogue to the $4f^1$ configuration of Ce [49]. We do not think so, a similarity exists, however, as Ce can have two valences 3 and 4 and Pu can also exist in two valences 2 and 3 (mixed valence: two (or more) integer valences as in Fe_3O_4) and just like Ce compounds can also be intermediate valent (quantum mechanical hybridization of two valences, resulting in one non-integer valence, e.g. 2.5) (but see below). The neighboring actinide compound $NpCoGa_5$, however, is an antiferromagnet with a $T_N = 47$ K [50]. However, band structure calculations by Ophale and Oppeneer [44], assuming as starting point for their ab initio calculations itinerant $5f^5$ electrons in $PuCoGa_5$, find long-range antiferromagnetism. Then the starting assumption must be questioned.

Experimentally, however, susceptibility measurements reveal a Curie–Weiss behavior at elevated temperatures with effective moments corresponding to a $5f^5$ configuration, but with an extrapolation to a negative paramagnetic Curie temperature of $\theta_p = -3$ K [5]. *Thus there are certainly antiferromagnetic fluctuations or short-range order such as clusters, etc.*

Now we should discuss the special role of Pu within the actinide series. It has been shown [51] that the actinides and their compounds or alloys are the high-pressure phase of the corresponding rare earth compounds or alloys due to the more delocalized 5f states than the 4f states. Thus, Pu is at the position of Sm and Sm does exist in two valences: semiconducting divalent $Sm^{2+}S^{2-}$, mixed valent semiconducting $Sm_3S_4 - Sm^{2+}Sm_2^{3+}S_4^{2-}$, intermediate valent high-pressure $Sm^{2.8}S + 0.8$ electrons with hybridization gap and semimetallic $Sm^{3+}N^{3-}$. PuS, PuSe, PuTe as high-pressure phases of the corresponding Sm chalcogenides indeed are intermediate valent as UPS and other measurements [51] have shown [52,53]. Sm^{2+} and Pu^{2+} have also a non-magnetic $^7F_0$ $J = 0$ configuration in common. Is Pu in $PuCoGa_5$ really only Pu^{3+}, or mixed valent Pu^{3+} and Pu^{2+} or even intermediate valent?

Here, we have to resort to a recent UPS photoemission spectrum on $PuCoGa_5$ [48]. Regarding the question of localized versus band 5f states, we have to recall that photoemission (PE) measures final state spectra, i.e. a f^n localized initial state results in the f^{n-1} multiplet as final state and a delocalized band as initial state yields the density of states of this band. This has been extensively shown on rare earth compounds [54], where the 4f states are generally localized. Intermediate valence due to hybridization is broken up at the site of the photon absorption and decomposed into the final state multiplets of the two constituents, because the energy of the incident photon is so much higher than the hybridization binding energy of the intermediate valent state (about 10–100 meV).

In Fig. 8, we show the PE spectrum of $PuCoGa_5$ measured on laser ablated single crystals at 77 K [48]. The spectral resolution was 75 meV. The spectrum exhibits a sharp structure at E_F and a broader feature centred at -1.2 eV below E_F, both being superimposed by a broad Co 3d
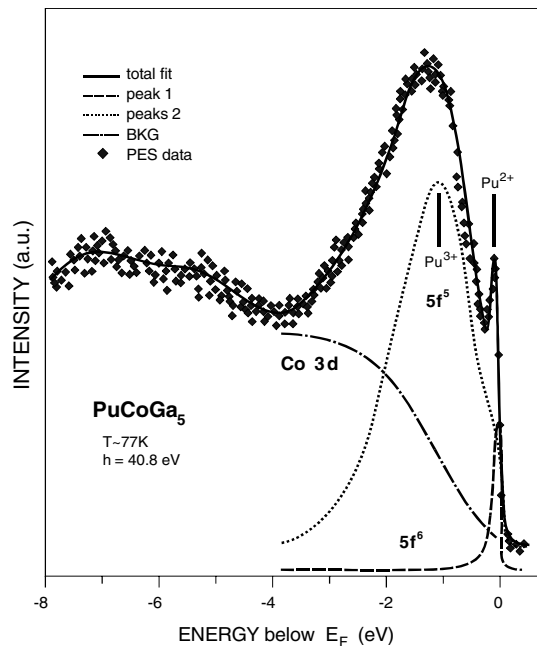

Fig. 8. UPS results on $PuCoGa_5$ single crystals at 77 K and their decomposition into Co3d and $5f^5$ and $5f^6$ contributions. Spectral resolution, 75 meV (after [48]).

band. As variation of the photon energy shows both peaks have 5f character. The authors prefer for the explanation a mixed level model (MLM) where one 5f electron (at E_F) is delocalized and four 5f electrons (near -1.2 eV) are localized, but all belonging to the same $5f^5$ configuration. In view of what we said above about final state multiplets, we cannot find such structures in the PE spectrum related to the localized states. Maybe they are smeared by superposition or hybridization with the 3d band. However, in the PE spectrum of intermediate valent PuTe or PuSe, these structures are present [52,53]. The MLM is a theoretical concept where multiple peaks in a spectrum can always be fitted by permitting some f electrons to be localized and others delocalized and then minimizing the total energy of various interactions, those which one can think of and those which one can treat. There will always be a minimum in energy, but why 1:4 instead of 2:3 or 2:2:1, is not known. One has a new fitting parameter, which bears little relevance to reality.

We think that Fig. 8 has the classical appearance of a mixed valence situation with Pu^{3+} and Pu^{2+} *narrow f bands*, both extending towards E_F, conspicuously 1.2 eV apart, similar as the various Cu valences. A comparison with the XPS spectrum of Fig. 1 for the mixed valent Cu situation in LaSrCuO helps to understand. There the majority ions with spin 1/2 are the Cu^{2+} ions yielding the dominant PE peak and on the higher binding energy side is the minority Cu^{3+} peak, separated by about 1 eV. Since the spectral resolution was with 0.8 eV much worse than the 75 meV in Fig. 8, the 2 Cu peaks are not completely separated. For Pu in Fig. 8, the majority ions are Pu^{3+} with $J = 5/2$ yielding the dominant peak at -1.2 eV below E_F.

Minority divalent Pu^{2+} must be situated at the lower binding energy side, i.e. closer to or at E_F. The integrated intensity of both peaks yields about 10% Pu^{2+} with respect to Pu^{3+}. Further evidence of the mixed valence situation is that the dominant magnetic Pu $5f^5$ peak (at -1.2 eV below E_F) has a much larger line width than the nonmagnetic Pu^{2+} $5f^6$ peak at E_F, probably due to magnetic exchange interactions. *This is identical as in Fig. 1 for the magnetic and nonmagnetic Cu peaks.* It is also evident from Fig. 8 that there is some hybridization between both $5f^5$ and $5f^6$ configurations, probably mediated by Co 3d states.

But Pu^{2+} is a spin hole with respect to the dominant Pu^{3+} magnetic ions and the argumentation is the same as for the Cu mixed valent situation. However, Pu^{2+} has one electron more than Pu^{3+}, thus the conductivity is n-type: *the spin holes prevent the long-range antiferromagnetism in $PuCoGa_5$, thus only antiferromagnetic clusters with short-range order exist.* It is quite clear that this situation is now the same as for the Cu HTSC and the argumentation regarding the magnetic binding energy is the same [10,27]. The origin of the ferrons or magnetic polarons is as depicted in Fig. 3, the nonmagnetic bipolarons being bound by 2 times the magnetic exchange energy. On the other hand Pu^{2+} is larger in diameter than Pu^{3+}, so there exists also a ferro-distortive lattice distortion around the bipolaron, which contributes to the binding energy. But at the same time the nonmagnetic bipolarons are also two electrons, in this case, which couple with the phonons in a BCS manner. This, however, leads only to a T_c of 2–3 K. An isotope effect on $^{239}PuCoGa_5$ and $^{242}PuCoGa_5$ has been sought for, but not been found, mainly due to the different radioactive decay of T_c for the different isotopes [55].

We then need also a pseudo-gap temperature T_p of the antiferromagnetic clusters. NMR measurements [43,56] yield a spin-fluctuation energy T_p of 260 K, corresponding to a spin gap. But also a resistivity measurement exists, just as for the 124 Cu single crystals [33,43]. The resistivity for $PuCoGa_5$ above T_c is not at all linear but exhibits a kink with a reduced slope above about 250 K [43]. Similar as in 124 this kink is at the same temperature where NMR and Hall effect [32–34] found the pseudo-gap, *so we can take this kink in the resistivity of $PuCoGa_5$ at 250 K as the opening of the spin pseudo-gap and thus the ordering temperature of the antiferromagnetic clusters.*

We then have to assume that the nonmagnetic bipolarons make a Bose condensation at $T_c = 18.5$ K. As we have argued before, a classical Bose condensation should be gapless and the specific heat at low temperatures should not be an $\exp(-\Delta/k_B T)$ law, but rather a T^3 power law [29,37]. The specific heat of $PuCoGa_5$ has been measured and corrected for the lattice contribution with the corresponding U compound [43]. C/T versus T between 5.2 and 10 K shows a curvature, in spite of the fact that the authors of Ref. [43] fit a straight line between $5.2 < T < 7.2$ K, insinuating a T^2 law. But using the temperature interval $7 < T < 10$ K, one finds an exponent near

3, i.e. a T^3 law. The lowest temperatures are always very sensitive to temperature correction due to the self-heating process during the radioactive decay. *In any case a power law is fulfilled as Bose condensation demands*, *instead of the exponential law.*

NMR measurements further show [56] that one has a spin singlet superconductor and the symmetry of the orbital component of the wave function must be symmetric, so L must be even as for s or d wave. But there is a good indication that the spin susceptibility is not going towards zero for $T \rightarrow 0$, but that there is scattering from states within the gap. The authors of Ref. [56] conclude that the gap has nodes as for d-wave pairing and that the superconductivity is unconventional and dominated by antiferromagnetic fluctuations.

4. Conclusions

In this paper, we compare significant experiments of Cu HTSC with equivalent measurements on "high T_c" $PuCoGa_5$. Whereas for the Cu SC, the mechanism for superconductivity is still discussed even today, the actinide community unanimously agrees that antiferromagnetic fluctuations, short-range order and magnetic exchange energy are the main reasons for "high T_c" superconductivity [5,6,43,48,50,55]. It is a fact that none of the Cu and Pu superconductors show long-range antiferromagnetic order in spite of the fact that antiferromagnetism does not inhibit superconductivity [45,46]. Nevertheless, in all materials spin pseudo-gaps have been observed which necessitates at least antiferromagnetic short-range order, e.g. in clusters.

All Cu and Pu superconductors are of mixed valence as photoemission data have shown [9,10,48]. The majority ions are magnetic, the minority ions are nonmagnetic and act as spin holes. These spin holes in a concentration of about 10% dilute the antiferromagnetic order so that only short-range correlations remain. Two-dimensionality is not essential [23], but it helps. n or p type conductivity is not important.

It is clear that in the Pu alloys only Pu f states sit at or near E_F [48] and are involved in superconductivity. This strongly supports the model that in the Cu superconductors there are also the cation Cu ions and not the O anions which are responsible for superconductivity. In Mott's model [29–31] there is no spin gap and no ordering temperature, the Cu ions away from the O^{1-} ions "resonate" (nobody has ever found a resonance frequency). Such a model cannot work in the Pu alloys. *However, the models of de Jongh [27,28] and Wachter and Degiorgi [10], where a spin hole in an antiferromagnetic matrix creates ferrons with mutual attraction to form nonmagnetic bipolarons, work both for the Cu and the Pu superconductors. These bipolarons form already above T_c and undergo a Bose condensation at T_c. Since these magnetically coupled nonmagnetic bipolarons always are also charge pairs with two electric charges which distort the lattice, a coupling to phonons as in the*

BCS model will also exist, but this is not the main binding energy of these charge pairs and thus T_cs of high T_c superconductors can be expected.

The claim for a Bose condensation in Cu SC comes mainly from the experimental evidence of the two-fluid model: the f-sum rule, derived from optical absorption in the very far infrared [33] and the opening of a pseudogap in the electronic density of states as obtained from point contact spectroscopy [40]. On the other hand, both measurements show that the density of states never becomes really zero in the gap (in agreement with Ref. [38]) and this means a d-wave nodal gap function. This is also the case in the Pu superconductors, where the evidence comes from an analysis of NMR results [55]. The specific heat corroborates these ideas, inasmuch as neither for the Cu nor for the Pu superconductors the specific heat below T_c has the form of $\exp(-\Delta/k_B T)$ as for classical superconductors, but rather a power law because a Bose condensation is gapless.

Thus, we find in every respect that the Cu and Pu high T_c superconductors behave absolutely in the same way and thus must be explained by the same model.

At the end we may ask again what is so special about Cu that after 20 years of research only Cu compounds and nowadays Pu alloys are high T_c superconductors. As we have shown we need an element, which exists in at least two valences, one being magnetic (majority) and the other not (minority). For the actinides this is only Pu and to a lesser amount maybe Am. $AmCoGa_5$ is a low temperature superconductor with $T_c \approx 1.9$ K [57]. The basic magnetic interaction should be antiferromagnetic. The energy difference between the valences of both ions must be in the order of 1 eV. For the 3d elements in a compound, it depends on the crystal field in which magnetic state (high spin or low spin) the two valences are, e.g. in Fe_3O_4 both Fe ions are magnetic and the compound is ferrimagnetic. In general the simplest idea is to take the electron analogue of Cu, namely Ti with its two valences Ti^{3+} and Ti^{4+}, one magnetic, the other a spin hole. The author has prepared many compounds with Ti mixed valence, some were low T_c superconductors, but most were ferromagnetic. In any case no high T_c superconductor has been found.

Looking back at the history of the high T_c superconductors, we can risk the prediction that in the field of actinides only Pu compounds or alloys have the chance to become "high T_c" superconductors.

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