A Local-Pair Mechanism for High-Temperature Superconductivity at the Di -and Trivalent Sites

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Abstract

The p/d hybridization that primarily characterizes copper leads to local moments, lacking of the pair-breaking variety, both at di- and trivalent sites. Support for the negative-U model is extracted from the author's earlier work on the metal-insulator transition.

A more magnetically oriented model, like the resonant valence band model which we have recently associated with our observations in d1 TiOCl etc., does not really seem suited to the geometry and electronic conditions in the copper oxides present. However it is suggested that TiB_2, La_3S_4 and the Chevrel phases might be open to treatment by such a model.

Comment it also made about how the superconductivity of PdH_x and $Ba(Pb/Bi)O_3$ might be seen in the light of the present model, and attention is directed once again to what might be happening in the pressure-quenched CuCl and CdS.

1. Introduction

This text looks at several other unusual superconducting materials such as $Ba(Pb/Bi)O_3$ and PdH_x. It also probes further the mysterious behavior reported several times for suitably pressure-quenched CuCl, CdS and $TiBi_2$. The Allendar, Bray and Bardeen-type (ABB-type) model proposed for CuCl might be replaceable by a simpler and less structured one.

The final section in the text assesses of the proposed negative-U model in light of the preceding material. The requirements are such as to automatically make the occurrence of high-temperature superconductivity a great rarity. Copper (and possibly silver) mixed-valent oxides have very favorable and virtually unique characteristics, while $YBa_2Cu_3O_7$ possibly exists as a structure perfectly fitting to the requirements.

2. Real Pair Phenomena of the CuCl, CdS and TiB$_2$

Why the effects of the pair mechanism are commented upon here is because it was just such an unstable phenomena which made pressure-quenched CuCl [1] and CdS [2] at once so attractive. Wilson, in his discussion on CuCl, [3] attempted to produce a disproportionation and microphase-separation model that would permit an ABB-type [4] excitonic superconductive situation to arise. However, it has been wondered whether the ultra-dispersion of elemental copper liberated by the pressure treatment could not support prolonged fluctuations of the form

$$2s^1 d^{10} \rightarrow s^2 d^{10} + s^0 d^{10}$$

with the s^2 pairs giving rise to a Bose condensate.

For CdS it is found that the strange effects occur only if the sample is contaminated with chlorine to $\sim$1% [2]. If the effect of the pressure quenching is to transiently yield 'monovalent' $(Cd^2)^{2+}$, analogous to the mercurous ion $(Hg^2)^{2+}$, then the effect could again be associated with s^2 pairs, either in the M-M bands or through the disproportionation

$$2Cd^{1+} \quad \rightarrow \quad Cd^0 \quad + \quad Cd^{2+}.$$
$$s^1 \qquad\qquad s^2 \qquad\qquad s^0.$$
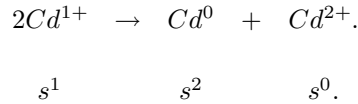
Perhaps the most remarkable (but least noted) work to come out of a military [4] laboratory was the work on titanium diboride TiB$_2$ [4]. This again may also represents local-pair supercondutivity as it has the AlB$_2$ hexagonal graphite-like net structure (though single bonds) with B atoms fully intercalated with one cation per ring, as shown in Fig.1. The compound contains ten electrons and is a low-carrier-density semimetal [5]. The figure illustrates the electron counting scheme whereby this can be understood. The two boron-based 2s bands are full with four electrons per formula unit. The boron p bands also form bonding and antibonding combinations. To just fill the former requires three electrons per boron: One from the borons themselves plus two per boron donated from the titanium. To this extent, TiB$_2$ is a four-valent titanium compound like TiSe$_2$. However, the anion sublattice in CdI$_2$-structured TiSe$_2$ is a simple quasi-ionic full-shell sublattice in which the holes of the semimetallic p/d Se/Ti overlap are 'independent' particles (prior to e/h pairing arising below 200 K [6]). In TiB$_2$, however, in the B-B bond sublattice the holes left by the semimetallic transfer of electrons back to the bottom of the Ti d band are conceivably driven there to associate and propagate as hole pairs, resonantly defining abandoned homopolar B-B σ-bonds. This situation is now much more like the situation proposed by Anderson [7, 8, 9] for the copper oxides; a model we suggested as inappropriate [6].
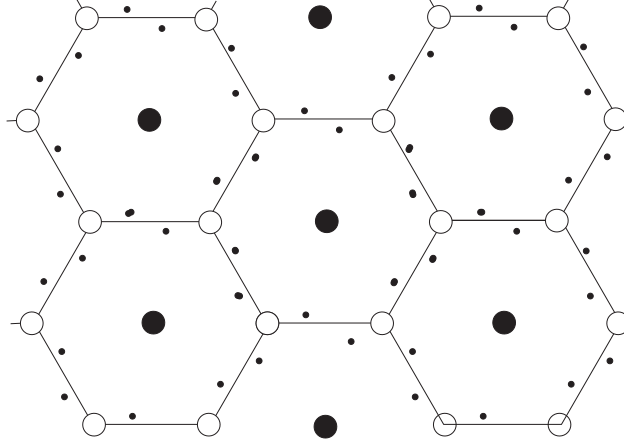
Figure 1. AlB$_2$-type structure of TiB$_2$ in plans, showing counting of electrons into B-B bonded hexagonal layer network. E$_F$ for the ten-electron system falls in the deep well in the density of states which separates the σ-bonding p states of the boron network from the empty band on the Ti sublattice. The virtually full p(σ) band takes six electrons; the deeper boron-based 2s bands hold the other four. Semimetallicity occurs through overlap of the p(σ) band with the Ti d band. Direct-space hole pairs in the σ-bonded B-B band would appear responsible for the superconductive manifestations. O, B; •, Ti; ., electrons of p(σ) band. Ti atoms lie halfway between the B sheets.

The difference between TiB$_2$ and non-superconductive semimetallic graphite is that the holes arise in TiB$_2$ in the σ-pairing band, but in graphite they arise in the p-band. In support σ-bonded semimetallic silicon at 150 kbar is a superconductor at 8.5 K [10], while the T_s for semimetallic black phosphorous is 11 K [11].

In the pyrite-structured semimetal SiP$_2$, as with graphite, the holes do not appear in the p(σ) bonding valence band, and no superconductivity (nor indeed e-h pairing) is observed [12].

The role of pressure [4] in the TiB$_2$ phenomena might be to adjust the semimetallic carrier content to a favorable value. The compound is likely to be non-stoichiometric.

3. Further Contrast and Parallels to What Occurs in the Copper Oxides

If one recaps the situation discussed in [13] and Fig. 2 for the quaternary copper oxide superconductors, following we have the mixed-valent situation;

$$d^9 + d^9 + \underline{d}^8 \rightarrow d^8 + \underline{d}^{10} + d^8.$$

In the more developed notation of Fig.1 this fluctuation became

$$^9Cu^0_{II} +^9 Cu^0_{II} +^8 \underline{Cu}^0_{III} \rightarrow^8 Cu^+_{II} +^8 Cu^+_{II} +^{10} \underline{Cu}^{2-}_{III}$$

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M(I)$_2$O M(II)O M(III)$_2$O$_3$

S S S

^{0}Ca$^0_{II}$

d(e$_g$)I

^{0}Cu^0_I ^{0}Sc$^0_{III}$ ^{9}Cu$^-_{III}$

d(e$_g$)II ^{8}Ni$^0_{II}$ o^{10}Cu$^-$ d(e$_g$)III ^{9}Cu$^0_{III}$ ^{10}Cu$^=_{III}$

^{9}Cu$^0_{II}$ ^{8}Cu$^0_{III}$ ^{10}Cu$^=_{III}$ (E$_f$)$_{II}$

p
0 1 2 3 4 5 6 7 8 9 10

K Cu
Neutral ^{0}M$_I$

^{8}Cu$^{+\Delta}_{II}$ ^{8}Cu$^0_{III}$ ^{9}Zn$^0_{III}$

p
0 1 2 3 4 5 6 7 8 9 10

CuScTi V Cr MnFeCoNiCuZn
Neutral ^{0}M$_{II}$

p
0 1 2 3 4 5 6 7 8 9 10

Sc Ti V CrMnFe Co Ni CuZn Ga

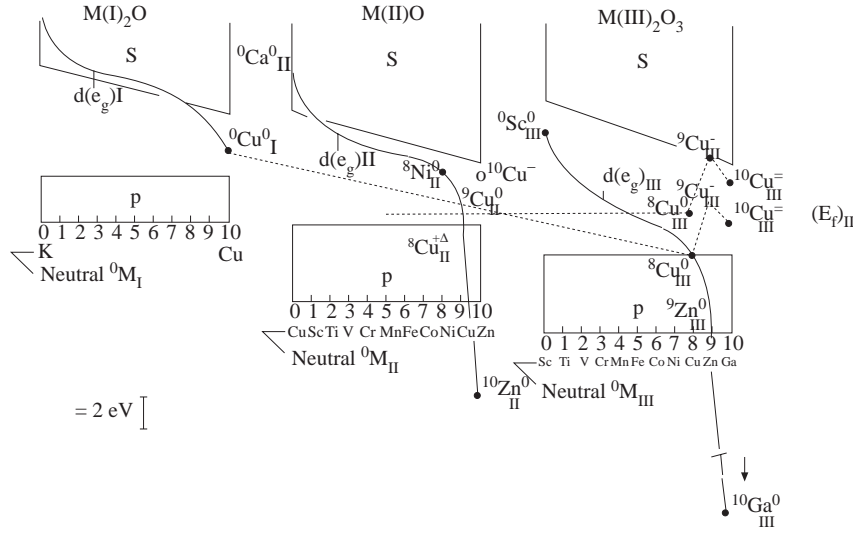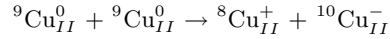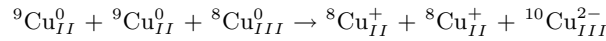^{10}Zn$^0_{II}$ Neutral ^{0}M$_{III}$

= 2 eV

^{10}Ga$^0_{III}$

Figure 2. Energy level diagram for binary oxides across the 3d series [13] used here to elucidate formation of negative-U centers in the mixed valent Cu(III)/Cu(II) oxides. The boxes give the energies of the main oxygen-based p valence band and cation-based s conduction band for pure (often hypothetical) mono-, di- and trivalent binary oxides across the 3d series. The curves give the approximate energy of the e$_g$ d band at the element concerned. The state notation carries information about the number of electrons on the cation, the element involved, its formal valence, and its overall charge condition away from that demanded by the formal valence. Thus ^{9}Cu$^0_{II}$ is the cupric ion, ^{10}Cu$^0_1$ the cuprous ion. The equation

$$^9\text{Cu}^0_{II} + {}^9\text{Cu}^0_{II} \rightarrow {}^8\text{Cu}^+_{II} + {}^{10}\text{Cu}^-_{II}$$

represents a metallic charge fluctuation for Cu$_{II}$. The equation

$$^9\text{Cu}^0_{II} + {}^9\text{Cu}^0_{II} \rightarrow {}^8\text{Cu}^0_{II} + {}^{10}\text{Cu}^0_{II}$$
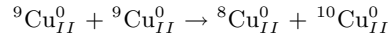
represents bulk disproportionation (not favorable here). The equation

$$^9\text{Cu}^0_{II} + {}^9\text{Cu}^0_{II} + {}^8\text{Cu}^0_{III} \rightarrow {}^8\text{Cu}^+_{II} + {}^8\text{Cu}^+_{II} + {}^{10}\text{Cu}^{2-}_{III}$$

represents the dynamic formation of the negative-U center (see text). The underlining of ^{8}Cu$^0_{III}$ etc, registers that a site in LSCO or YBCO is in a mixed-valent environment, and not so tightly bound as binary ^{8}Cu$^0_{III}$ etc. The negative-U situation with ^{10}Cu$^{2-}_{III}$ more stable than ^{10}Cu$^-_{II}$ leads to 'stable' pair formation. The effect follows from the high stability of the ^{10}Ga$^0_{III}$ trivalent closed shell. This notation has been presented here for those who in this field have only time to read figure captions. Further discussion appears in the text.

The role of the doping in $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ (LSCO) is to produce the sites $_8$Cu$^{2+}_{III}$ driven towards trivalency which feature in [14]. In YBa$_2$Cu$_3$O$_7$ (YBCO) [15] these sites are those with the square-planar coordination.

The possibility of local pairing has surfaced before in mixed perovskite $Ba(Pb/Bi)O_3$ [16]. In pure $BaBiO_3$ there occurs the expected drive towards semiconductivity through a disproportionated charge-ordered state [17], since $Bi^{4+}(s^1)$ is not a stable valence. For the full dispropotionation $2s^1 \rightarrow s^2 + s0$ we can write correspondingly

$$^1Bi^0_{IV} +^1 Bi^0_{IV} \rightarrow^2 Bi^0_{III} +^0 Bi^0_V.$$
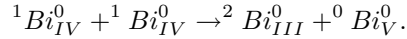
However in the Pb/Bi mixed material with less than 30% Bi, crystallographic charge-ordering is not affected and we retain a more quadrivalent environment [18], so that one might write

$$^1Bi^0_{IV} +^1 Bi^0_{IV}(+^0Pb^0_{IV}) \rightarrow^2 Bi^-_{IV} +^0 Bi^+_{IV}(+^0Pb^0_{IV}).$$
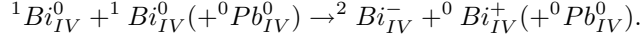
Here the electron pair is less lattice-coupled and therefore free to propagate and even to Bose condense as a pair. Superconductivity in $Ba(Pb/Bi)$ O_3 has its maximum T_s ($\sim$12 K) just prior to loss of the disordered perovskite structure at $\sim$30% Bi. This is the highest T_s for any non-transition-metal compound. Carriers are beginning to show localization just as in the copper oxides [19], and again $N(E_F)$ is small.

Note the disproportionation of the $BaBiO_3$ is triggered by the full, relatively narrow s^2 lone-pair band, familiar in compounds like PbO and BiI_3. When the s band is open (i.e. nominally s^1, as in β-InTe or SnAs) it is much wider. The superconductivity both of rocksalt β-InTe and SnAs is susceptible also to representation as above, but there is heavy p/s mixing in these materials and T_s is low (3.5 and 3.6 K respectively) [20]. (Note α-InTe is a charge-ordered semiconductor with TlSe structure.)

In the realm of strange superconductors we find PdH_x:Ag with $T_s = 17$ K and a positive isotope effect ([21] and reference therein). This again can be represented as a closed shell effect. PdH should not be considered as a pseudo-halide like $LaH3$ but as a material analogous to CsAu, in which charge transfer is to the Pd to complete the d band. We then have the following approximate configurations: Pd, s^1d^9; Hpd, s^1d^{10}; H-defective cells, s^0d^{10}; Ag-doped cells, s^2d10. The presence of s^0, s^1 and s^2 sites makes this look like $Ba(Pb/Bi)O_3$ again. The roller of the Ag is probably to act as a band-narrowing agent.

The Chevrel phase $Pb^{2+}[Mo_6S_8]^{2-}(T_s \approx 15K)$ would seem more of the nature of TiB_2. Now electron counting is such that 16 electrons are required to fill the sulphur p bands : two are drawn from the Pb and 14 come from the six Mo, which initially have a total of 36. The 22 remaining on the octahedral Mo_6 cluster are two short of satisfying the 24 required by the 12 Mo-Mo bonds of the cluster. The deficit in part supplied by the lone-pairs s electrons still on the Pb. A metal is formed in which hole pairs might propagate through the Mo_6-cluster sublattice over 'lost' homopolar bonds, as was suggested for TiB_2. Thallium and indium also can play the role of lead (or tin), as can trivalent rare-earth metals [22], but with alkaline earths or with divalent Eu there is no superconductivity.

Without much detail at this point may we point out that the superconductivity in the chain-structured p/d semimetal $TaSe_3$ could be due to hole pairs in the top of the

very weakly bonded Se-Se pair band associated with the red chain ([22] and references therein).

We would now like to turn to other ternary and quarternary superconduting transition metal oxides, since these potentially come closest to resembling $(La/Sr)_2CuO_4$ and similar species.

This is a shear-structure-type molybdenum bronze with a superconductive onset of 2 K [23]. The valence and structural disorder encourages localisation in the molybdenum sublattice prior to superconductivity. The mixed-valent situation is $3Mo^{6+}(d^0) + 3Mo^{5+}(d^1)$ and defective $d^1 - d^1$ pairing could be responsible both for the incipient localization and the superconductivity. In the stoichiometric shear structure of $Ti_4O_7(2Ti^{4+}(d^1))$ comparable pairs at low temperature charge-order on the lattice and non-metal results [24]. However besides being disordered the 4d system is also more delocalised, so that the structure does not distort to trap the pairs. This also seems to be the case with La_3S_4 $(T_s = 8 K)(2La^{2+}(d^1) La^{3+}(d^0))$.

The case of $LiTi_2O_4$ is a mixed-valent spinel with a T_s of 12 K. As for TiO_7, it has a 50/50 mix of Ti^{3+} and Ti^{4+}, but now the two are crystallographically restrained to one site type [25]. This, plus the fact that some Li excess also occupies these sites, prevents the system from charge ordering, and again a plausible cause of superconductive state forming is fluctuating M-M pair-bonds [26].

The above d^1/d^0 systems are clearly different from the copper oxide circumstances in that the t_{2g} wavefunctions are involved, which opens the way to M-M pair bonding between sites.

Perhaps a slight tendency to onsite real-space pairing occurs in these 7 K superconductors. Their trigonal prismatic coordination lends particular stability to semiconductive d^2 MoS_2, with its full, rather narrow, d_{z^2} sub-band. charge density waves and superconductivity compete in these d^1 layer metals [27].

This t_{2g}^5 low-spin rutile metal might have correspondingly made use of fluctuations into t_{2g}^6, the full sub-band that brings semiconductive stability to so many compounds from Fes^2 to $CoAs_3$ [28]. There is no evidence, however, for superconductivity in IrO_2. It seems to be too good a metal: also the stability of t_{2g}^6 PtO_2 is not pronounced. Direct $t_{g2} - t_{2g}$ interactions in the 5d oxide are large [29]. Na_xRuO_2 could be more promising as a ternary mixed-valent system.

It ought to prove possible to dilute Ir^{4+} into some quaternary resembling $La_2(MgRu)O_6$, (which is a $GdFeO_3$-type ordered perovskite [30]) without the appearance of magnetism. If this can be doped further to generate some $Ir^{5+}(d^4)$ (as does occur in a variety of oxides, e.g. $Ca_2Ir_2O_7$, $Ba_{1/2}IrO_3$ [31]) we begin to have something which might mimic LSCO; namely $Ir^{5+}(t_{2g}^4)$ sites ready to take on pairs of electrons as stable $Ir^{3+}(t_{2g}^6)$ drawn in from the surrounding Fermi sea based on $Ir^{4+}(t_{2g}^5)$.

It is only when one contemplates manufacturing such a situation that one realizes how fortunate we have been to stumble across LSCO and YBCO and in relatively cheap copper compound at that! The one advantage possibly to be gained in shifting the search for improvement to 4d and 5d oxides is greater delocalisation. Remember that even $La(La_{1/4}Ba_{3/4})_2Cu_3O_{7+\delta}$ was not a metal, let alone a superconductor, despite its mixed

valence, while of course the majority of divalent copper oxides, like the now famous 'green compound' Y_2BaCuO_5 [32], are magnetic Mott insulators.

The now higher $p(\pi)$ band prevents totally any Cu^{III} being formed, and indeed severely restricts formation on Cu^{II}. The consequence is an abundance of formally Cu^{I}/Cu^{II} mixed sulphides like KCu_4S_3, $K_3Cu_8S_6$ and KCu_3S_2. These particular chain-structured metals show CDW and are not superconducting [33]. CuV_2S_4 shows CDWs too, while $Cu\,Rh_2S_4$ is superconducting standard.

4. Conclusions

Now with regard to several of the materials discussed in this text, it does seem that the possibility might exist, particularly in broader band materials, for a local-pair condensate to occur that actually runs as the negative-U (here, hole) centers themselves, more in the manner suggested by Anderson's recent resonant-valence bond model. This is especially likely in those semimetals with broken homopolar bonds, such as TiB_2, $PbMo_6S_8$ and high-pressure Si, P and S. In this regard we would suggest that the situation in TiB_2 be examined very closely since it is defintely an unusual physical and crystallochemical situation.

The general conclusion of this examination of the more chemical aspect of what is happening in the quaternary copper oxides is that the remarkable combination of properties that open the way to high temperature superconductivity stem largely from one fact-the near-closed- shell electron content of copper. This has the following effects: (I) it places the d band low in the map $p \rightarrow s$ gap which causes heavy p/d hybridisation; (ii) this ensures the absence of magnetism both from Cu^{II} and Cu^{III} in these oxides; (iii) it further gives rise to bands which, though fairly narrow, are metallic yet not magnetic; (iv)it yields ions which are small and not susceptible to M-M bonding; (v) it gives ions that can accept a wide range of coordination geometries; (vi) it involves the very strong $d^9(e_2^3)$ Jahn-Teller configuration; (vii) it sees, as with d^1, the generation of a Fermi surface of simple geometry; (viii) above all it encourages disproportionation, and opens the way to the formation of single coordination unit negative-U centres. Without the majority if not all these aspects there would be no high T_s in $(La/Sr)_2CuO_4$. What makes $YBa_2Cu_3O_7$ still more remarkable is that it wants to form and moreover to order its mixed-valent Cu sites into a layer structure. That caps favourable circumstances by sheer good fortune.

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