

# Electride Chemistry and Unassociated , Free Electrons : A Possible New Approach to High Temperature Superconductivity

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The electron physics of metallic solids governs the appearance (or not) of superconductivity in them , and limits the transition temperature of the superconducting state in the relative few in which this phenomenon is observed . In the following presentation an entirely different approach to achieving superconductivity in materials is proposed : new **nonmetallic** compounds are designed in which the conduction electrons , located in large void spaces in the lattice , are entirely free of , and unassociated from their parent atomic kernels . These latter electrons would resemble those in electrostatic and related phenomena . Electride chemistry is an appropriate technique to produce the new materials containing such free , unassociated electrons located in lattice void spaces . If those solid state electriles are physically and chemically stable at high temperatures , and if the electrons can flow through the void channels unimpeded , the proposed electrile compounds should be superconducting at those elevated temperatures .

## About Electrons

In this new “electrostatic superconductivity”, two types of electrons are recognized : electrons associated orbitally with their parent atomic kernels , and free electrons which are unassociated with them . The electrons associated orbitally with their parent atomic kernels are located in the the inner and outer (valence) atomic electron shells , localized pairs of valence shell electrons (covalent bonds , inert/lone pairs) , and the delocalized valence shell electrons in metallic bonds/conduction bands .

Free electrons unassociated with any particular atom are found in many types of static electricity : that annoying “static cling” and crackling

discharges from textiles in dry air , especially in Winter ; the spectacular natural discharges of static electricity in lightning bolts from storm clouds ; artificial lightning bolts from a Tesla coil (from a laboratory vacuum tester) ; electrical arcing from breaks in an electrical circuit (such as a fallen power transmission line) ; and the flow of electrons through the vacuums of fluorescent tubes and CRT television sets (or of old computer monitors , like the one on which I'm typing these words) . The electrons in these electrostatic phenomena are all located on the outside of atoms and molecules , either bonded to them by van der Waals dipolar bonds (textiles , storm clouds) , or being impelled through a vacuum or air by a very high voltage across a pair of electrodes (Tesla coil , fluorescents , CRTs) . These electrostatic electrons are entirely free and are unassociated with any specific atom .

The two general classes of electrical conductors are :

- \* Ionic conductors such as molten salts at high temperatures , fast ion conductors like  $\beta$ -alumina and  $\text{Cu}_2\text{HgI}_4$  , and solutions of ionic compounds in aqueous and non-aqueous solvents ; and ,
- \* Electronic conductors whose charge and energy carriers are electrons in the orbitals comprising the metallic bond/conduction band in the crystal ; these are the conventional metallic solids .

A third , overlooked class of electrical conductors can also be included : that of the unassociated , free electrons , as they travel through the air or vacuum between regions of high and low electrical potential . A typical lightning bolt can undoubtedly transport a huge amount of electrical charge and energy from its host rain cloud to the ground below .

The electrons in the orbitals comprising the metallic bond/conduction band of a metallic solid are subject to Fermi-Dirac statistics (the “Fermi-Dirac distribution”) because of their quantum nature [1](#) . This organization of the mobile conduction electrons in vast numbers of energy levels within the metallic bond pairs most of them in levels of increasing energy ; typically about 1% remain unpaired , as singlets , above the Fermi level ( $E_F$ ) [2](#) .

Since superconductors are entirely diamagnetic in nature these last remaining singlet conduction electrons must be paired for the metal to enter the superconducting state . At the higher energy levels of the metallic bond they are scattered across the physical dimensions of the lattice with increasing separation distances . It's therefore very difficult to complete the pairing of the singlet electrons above  $E_F$  into the Cooper pairs required for superconduction in the material . As a result , relatively few elementary metals – twenty-nine of them [3](#) , under ambient pressure – are known to superconduct , and then only very close to Absolute Zero .

In order to achieve higher transition temperatures for superconducting materials , some sort of physical or chemical “trick” must be used by the researcher . The first class of genuine high temperature superconductors discovered , the cuprates , benefited from such an enabling mechanism . It was originally attributed to the “chemical pressure” in the lattice from undersized interlayer Rare Earth cations , but more likely high  $T_c$  superconductivity in the cuprates resulted from antiferromagnetic (AFM) induction from the highly AFM copper oxide host lattice [4](#) .

The most useful and productive “trick” for designing and synthesizing new high temperature superconductors may be the most radical one yet proposed : simply avoid the Fermi-Dirac distribution in the metallic bond . Since the metallic bond is comprised of a lattice-wide molecular orbital (“crystal orbital”, [5](#)) containing associated electrons , it will always be affected by the Fermi-Dirac distribution . Therefore , the new electronic materials proposed in this essay won't have a metallic bond with its associated electrons . Instead , unassociated free electrons will be the charge and energy carriers in them . The new materials containing such free electrons will be electrides , and the synthesis methods of electride chemistry will be proposed for making them .

## About Electrides

Electrides have been known for over two hundred years , having been first discovered in 1808 by the English chemist , Sir Humphry Davy [6](#) . Such strange and fascinating electronic materials have attracted the attention of many scientists since then . An immense research literature about electrides has accumulated , especially in the past few decades , with numerous reviews on the topic being available [7](#) .

An electride is commonly defined as an ionic compound in which the anion has been replaced by an electron [8](#) . Alternately , it can be considered from a more general “synthesis point of view” : an electride is a compound formed by the insertion of a zerovalent metal guest atom into a compatible host lattice , with the location of the guest atom’s parent cationic kernel and one or more of its valence shell electrons in separate , adjoining compartments or regions of the host’s structure .

The latter description of electrides implies a net energetic stabilization of both the guest’s cationic kernel and its separated electron(s) within the host’s compartments . The first – and probably most studied – electride system is that of sodium metal dissolved in pure , anhydrous liquid ammonia . Sodium is a powerful reducing agent with a very high standard oxidation potential ( $E^0_{\text{ox}} = 2.71 \text{ V}$  at STP versus the SHE) ; that is , sodium atoms are extremely energetic . They can greatly reduce their energy content by donating their  $3s^1$  valence electrons to the host ammonia molecules . The electrons are said to have been “solvated” by the ammonia ; they are thought to form weak van der Waals dipolar bonds with the positive ends of the ammonia molecules’ dipoles [9](#) .

The sodium cations , which have the electronically very stable neon  $2s^2 2p^6$  octet , are also energetically stabilized in the solution by forming feeble coordinate covalent bonds with the host ammonia (approximately 6  $\text{NH}_3$  molecules per  $\text{Na}^+$  cation , octahedrally coordinated) .

The resulting sodium–ammonia electride is a very reactive reducing agent , and indeed Alkali metal electrides have found applications in chemical

syntheses as “dissolving metal reducing agents”, such as in the Birch reduction of certain organic compounds . The high energy of the original sodium metal atoms is still present in the electride solution . However , the “point source” energy concentrated in the individual sodium atoms has now been transferred to , and dissipated throughout the volume of the electride solution . Such an energy dispersal is highly favorable thermodynamically , and is the engine that drives the chemical reaction in which the solution of sodium–ammonia electride is formed .

Solutions of the Alkali and Alkaline Earth metals (except beryllium [10](#)), and of europium and ytterbium [11](#), in ammonia and in various amines and ethers were for a long time the only known electride systems . In recent decades two new classes of electrides have been devised and investigated : first , **organic electrides** , mainly the invention of Dye and co-workers [12](#) , in which the parent metal cation is complexed by an enveloping organic ligand such as a crown ether or cryptand . Addition of the complexing ligand promotes the electride formation as it energetically stabilizes the cation component . The separated valence electrons from the guest metal atoms are stabilized in cavities and channels in the lattice of the crystalline electride by polar bonding with the “image positive charge at the center of the cavity” (Dye , [6](#) , p. 1567) .

The second new class of electrides is that of the **solid state inorganic electrides** , developed mainly by Hosono and co-workers . Two types of host structures have been studied for these compounds : zeolites , with their large aluminosilicate shells [13](#) , and more recently , a complex calcium aluminum oxide [14](#) , which also has spherical volumes for containing the highly reactive free electrons separated from the guest metal atoms . Electrides formed by the dissociation of Alkali metal atoms in the interstices of silica zeolites and in silica gel structures have also been studied (Dye , [6](#) , pp. 1569–1570) .

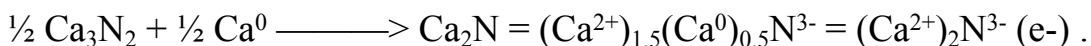
Solid state inorganic electrides will be the focus of this essay , although a brief section on organic electrides will be included at the end of the presentation . Before proceeding to a survey of the proposed new type of electrides it might be useful to consider dicalcium nitride ( $\text{Ca}_2\text{N}$ ) and Hosono’s calcium aluminum oxide electride . These two compounds are

instructive examples of what to **avoid** in the design of the new electrides with unassociated free electrons .

## About Synthetic Metals and F-Centers

Dicalcium nitride (also called “calcium subnitride”) was first prepared in 1963 , and has been examined in several studies since then . Keve and Skapski (1966 , [15](#)) determined its crystal structure as the anti-cadmium chloride type , which was confirmed by Gregory and co-workers (2000 , [16](#)) . The latter researchers also found  $\text{Ca}_2\text{N}$  to have a metallic type of electrical conductivity , although it was only  $0.2 \text{ ohm}^{-1}\text{cm}^{-1}$  at 293 K (their Table 5 , p. 1640) . The compound also exhibited a weak Pauli paramagnetism , typical of many metallurgical metals . The  $\text{Ca}_2\text{N}$  samples synthesized in these studies were described as “dark greenish-black”, “lustrous”, and “graphitic” in appearance .

The original preparation of dicalcium nitride involved the insertion of calcium metal atoms into the normal nitride ,  $\text{Ca}_3\text{N}_2$  :

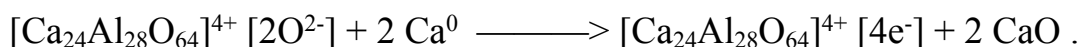


The “extra” electrons are resident in the van der Waals interlayer zones between the Ca–N–Ca slabs . For this reason  $\text{Ca}_2\text{N}$  has been considered as an electride (eg. Lee and co-workers , 2013 , [17](#) ; Walsh and Scanlon , 2013 , [18](#)) . In contrast to the rather low electrical conductivity of  $\text{Ca}_2\text{N}$  measured by Gregory et al. , Prof. Hosono’s group determined the material had the remarkably high conductivity (single crystal) of  $357,143 \text{ ohm}^{-1}\text{cm}^{-1}$  at 300 K ([17](#) , p. 2) , and around one million  $\text{ohm}^{-1}\text{cm}^{-1}$  at 10 K (their Figure 2b , p. 3) .

These properties of dicalcium nitride point to it being a Robin-Day Class IIIB mixed-valent compound ([19](#)) and a **synthetic metal** (refer to Figure 1 , “Physical Properties of Mixed-Valent Compounds”, p. [35](#)) . This is probably the most appropriate classification of  $\text{Ca}_2\text{N}$  as a chemical compound . The metallic bond in the material is likely similar to that in the parent calcium metal , that is , the 4s,p conduction band . Calcium never

becomes superconducting at any temperature , and apparently dicalcium nitride never does , either . In both metallurgical and synthetic metals the conduction electrons are associated with their parent atomic kernels in the lattice-wide crystal orbital (metallic bond , conduction band) . They are thus subject to the Fermi-Dirac distribution , which inhibits the formation of the Cooper pairs required for superconduction .

The most recent solid state inorganic electride , and one which has attracted considerable attention from researchers , is based on a calcium aluminum oxide substrate . It's structurally a type of zeolite , having periodic arrays of voluminous , roughly spherical chambers or “cages” (Matsuishi and co-workers , 2003 , [20](#) , Fig. 4A , p. 629) . Each unit cell of the compound has twelve cages , four of which are occupied by singlet electrons . The material was prepared by a somewhat awkward and inefficient [21](#) metathesis route by the replacement of two formula oxides in the calcium aluminum oxide precursor (C12A7) by four electrons :



Various reducing agents , including hydrogen (calcium metal in the above equation) were examined for removing the two excess oxides and replacing them with electrons . “The surface of the Ca-treated C12A7 was mechanically polished to remove the CaO layers before measurements” ([20](#) , p. 627) . The singlet electrons were found to have a strong antiferromagnetic coupling , forming anionic bipolarons which were coulombically bonded to the surrounding cationic lattice . They were able to hop from cage to cage , somewhat like the ionic conductors mentioned above on page 2 :

“The injected electrons are captured in the cages and behave like an anion with a spherical 1s wave function of an  $\text{F}^+$ -like center . They migrate throughout the crystal as a polaron , which thereby enhances electronic conductivity up to  $\sim 100 \text{ ohm}^{-1}\text{cm}^{-1}$  at 300 K . The electron anions exhibit spin correlation of antiferromagnetic coupling , forming a diamagnetic pair or singlet bipolaron” ([20](#) , p. 627) .

R.W. Pohl (around 1938 [22](#)) produced the first F-centers in Alkali metal

halide crystals by X-ray irradiation ; he called them “Farbenzentren” (“color centers”) . F-centers can also be formed in halide salts by doping them with the zerovalent parent metal atoms (for example ,  $\text{Na}^0$  in  $\text{NaCl}$ ) . Such halide F-centers are anion vacancies containing singlet electrons resonating around the cavity in the frontier orbitals of the host cations , which in the case of the  $\text{NaCl}$  F-center (having an orange-yellow color) are an octahedron around the singlet electron :  $\text{Na}^0(\text{Na}^{1+})_5 = (\text{Na}^{1+})_6 [\text{e}^-]$  .

As the electrons are in a sort of “micro metallic bond” in the octahedron (sodium’s  $3s, p$  orbitals in the  $\text{NaCl}$  example) they are associated with the parent cationic kernels . In effect , the F-centers are dilute solutions of mixed-valent cations in a host lattice having metal cations corresponding to those in the electronically-active F-center itself . Because these mixed-valent sodium octahedrons are dissolved in the host  $\text{NaCl}$  lattice , they resemble Robin-Day Class **IIIA** mixed-valent compounds (Figure 1 , p. [35](#)) in which cationic metal clusters with M–M covalent bonds are surrounded by anions (eg.  $[\text{Mo}_6\text{Cl}_8]^{4+}$  ,  $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ ) , and  $\text{Nb}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$  .

The singlet electrons trapped in the anion vacancies of the salt crystals are coulombically bonded to their cationic containers , and could therefore be considered as **polarons** . This apparently was the case with the singlet electrons in Hosono’s  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4\text{e}^-]$  electride . They had a limited mobility , paired together as bipolarons , in the material’s lattice under an applied potential difference .  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4\text{e}^-]$  was found in 2007 to be superconducting at  $T_c = 0.2 \text{ K}$  (Miyakawa and co-workers , [23](#)) . The bipolarons were seemingly able to escape the ionic grip of their host lattice and transform themselves into Cooper pairs .

While synthetic metals and F-centers are fascinating research subjects in their own right , they are clearly unsuitable as any sort of superconductor candidate compound . Their conduction electrons are either associated with their respective atomic kernels , and are therefore subject to the Fermi-Dirac distribution (as in the synthetic metals) ; or , they are unassociated with any specific atomic kernel but are firmly bound to their surrounding cationic lattice as a polaron or in antiferromagnetically coupled pairs as bipolarons (as in the F-centers) .



Although superconductivity can occur in both types of materials , it does so only at temperatures close to Absolute Zero (for example , in the synthetic metal silver subfluoride ,  $\text{Ag}_2\text{F}$  , at  $T_c = 0.066 \text{ K}$  [24](#) , and as noted above , in  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4e^-]$  at 0.2 K) . The search for high temperature superconductors must abandon synthetic metals and F-center types of compounds and look elsewhere for more promising candidate chemical systems and host structures . Prof. Hosono concluded ,

“Thus , the present finding of the superconductivity in  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4e^-]$  implies that the “electride” is a promising material category for realizing an exotic superconductor” ([23](#) , p. 7271) .

Such electriles with free , unassociated electrons , but with a different design to avoid their F-center nature , will be proposed in the following sections of this essay .

## Wurtzite and Zinc Blende Electriles

It would be useful for me at this point in the essay to change to a personal style of narration .

In October 2014 I was studying the chemistry of inert pairs in inorganic compounds , with the aim of designing new superconductor candidate materials containing them . The inert pairs would be forced somehow or other into the frontier orbitals of the participating metal atoms , where they might form the metallic bond in the lattice .

Inert pairs of  $ns^2$  electrons are found in the valence shells of heavier post-Transition metal p-block elements (Figure 2 , p. [36](#)) . Inert pairs are characterized by a relative lack of chemical reactivity with oxidizers , and are always oxidized together and never as singlets . Conversely , the atomic kernels underneath the inert pairs are mostly quite strongly oxidizing in nature .

The case of mercury is particularly interesting in this regard . Its valence shell electrons are  $6s^2$  , which is also the inert pair in elementary mercury .

Mercury has a  $5d^{10}$  shell of electrons, but these seem to be “submerged” and are completely inaccessible to oxidizers, even to the strongest of them, fluorine [25](#). Because the  $6s^2$  valence electrons are an inert pair, mercury is barely able to function as a metal; it has only a very feeble metallic bond produced by a slight leakage of the  $6s^2$  electrons into the  $6p$  orbitals. As a result it's a liquid at STP (m.p.  $-39\text{ }^\circ\text{C}$ ), and is very low boiling (b.p.  $357\text{ }^\circ\text{C}$ ). Mercury is also quite volatile at room temperature, forming a heavy, colorless, toxic vapor. Its electrical conductivity of  $10,406\text{ ohm}^{-1}\text{cm}^{-1}$  at  $25\text{ }^\circ\text{C}$  indicates a low population of mobile electrons in its  $6s,p$  conduction band.

When cooled in liquid helium mercury becomes superconducting at around  $4\text{ K}$  [26](#). The  $6s^2$  inert pairs are “popping off” (separating from) the  $\text{Hg}^{2+}$  atomic kernels and are relocating in the atomic voids as Cooper pairs. Their “inertness” seems to give them a certain amount of immunity from the Fermi-Dirac distribution. Barium metal, whose valence shell electrons are also  $6s^2$ , is a very reactive Alkaline Earth element. The room temperature electrical conductivity of barium is  $20,000\text{ ohm}^{-1}\text{cm}^{-1}$ , but it never becomes superconducting at any temperature. Its  $6s^2$  electrons aren't usually considered to be inert pairs like mercury's; they seem to behave like the typical valence shell electrons in most metals.

I wondered if there was a “chemical trick” or technique by which mercury's  $6s^2$  inert pairs could be popped off its  $\text{Hg}^{2+}$  kernel into the interatomic voids at room temperature. Possibly if strongly nucleophilic anions were physically forced down around the  $\text{Hg}^0$  atoms the inert pairs would be displaced into the voids and the  $\text{Hg}^{2+}$  kernels would form strong  $\text{Hg-Nu}$  coordinate covalent bonds with the anions, thereby preventing the inert pairs from returning to their parent  $\text{Hg}^{2+}$  cations.

At that time I was considering the wurtzite and zinc blende structures as “crystal containers” for the inert pairs intended as Cooper pairs. One compound in particular, the double zinc blende  $\text{Cu}_2\text{HgI}_4$  [copper(I) tetraiodomercurate(II)] caught my attention. Because zinc blende (and wurtzite) compounds have the empirical formula  $\text{MX}$ , their structures must always have an **even** number of atoms. If the formula has an **odd** number of atoms the structure will compensate for it by adding an empty

void space to make up the missing formula atom . This happens with  $\text{Cu}_2\text{HgI}_4$  , whose formula can now be written as  $\text{Cu}_2\text{Hg}[\ ]\text{I}_4$  , where [ ] is a cation vacancy , which like the  $\text{Cu}^{1+}$  and  $\text{Hg}^{2+}$  cations is tetrahedrally coordinated by iodide anions (see Figure 3 , p. [37](#)) .

As mentioned above on page 2 ,  $\text{Cu}_2\text{HgI}_4$  is an ionic conductor at higher temperatures . Above  $70\text{ }^\circ\text{C}$  the compound's  $\text{Cu}^{1+}$  ,  $\text{Hg}^{2+}$  , and [ ] void components become randomly distributed in the iodide anion framework , and the  $\text{Cu}^{1+}$  cations can migrate through the lattice via the voids under an applied potential difference [27](#) .

The thought occurred to me : if the  $\text{Cu}^{1+}$  cations can drift through the voids under an applied p.d. , then **electron pairs** might be able to as well . If they can do so at ambient temperatures and above , then the material with such electron pairs in the void spaces would in effect be a room temperature superconductor . Might an analogue to  $\text{Cu}_2\text{Hg}[\ ]\text{I}_4$  with electron pairs in the void spaces be designed and synthesized ?

The target compound would have the zinc blende or wurtzite structure with an odd number of formula atoms , so it would be obliged to have a void space to make up the even number of formula components . One of the metal atoms would be  $\text{Hg}^0$  , so two of the M components must be reserved for  $\text{Hg}^{2+}$  and [\*\*] , where \*\* represents the “popped”  $6s^2$  inert pair of electrons . Silicon (IV) was chosen as the second M component of the double zinc blende or wurtzite , as it's guaranteed to always have a tetrahedral coordination to the X anions , at least under ambient and moderate pressures . **Important note** : [28](#) . Sulfide anions are known to be strongly nucleophilic in nature , in fact almost as nucleophilic as cyanide anions in the Spectrochemical Series . They should press down into the electrophilic  $\text{Hg}^{2+}$  kernel and bond strongly to it , thereby forcing the inert pairs into the large , empty void spaces set aside for them in the formula . Sulfide anions can also readily accept a tetrahedral coordination in many inorganic compounds .

The “chemical trick” used in designing the new zinc blende–wurtzites is to observe a strict 1 guest metal atom : 2 host compound stoichiometric ratio

in the formulation . The first equivalent of host substrate will absorb the cation of the guest atom after its valence electrons have been separated from it (as in all electrides) . The host–cation combination will then form into a new crystal structure which will establish the overall structure of the electride . The second equivalent of host compound will provide the vacancy for the “popped” electron pair . Its structure will “mimic” that of the dominant host–cation structure . The end result should hopefully be a double zinc blende–wurtzite having the formula  $(\text{host}-\text{M}^{2+})(\text{host}-[**])$  . In this case the host will be silicon(IV) sulfide ,  $\text{SiS}_2$  , so the material’s formula will be  $(\text{SiS}_2-\text{Hg}^{2+})(\text{SiS}_2-[**])$  , or  $\text{Hg}^{2+}[**]\text{Si}_2\text{S}_4$  . It should be isostructural with  $\text{Cu}_2\text{HgI}_4$  , ie,  $\text{Hg}^{2+}[ ]\text{Cu}_2\text{I}_4$  ; see Figure 4 , p. [38](#) .

Unlike the conduction electrons in the synthetic metals and F-centers , which are associated with the frontier orbitals of their parent atomic kernels , the pairs of electrons in the cation vacancies of  $\text{Hg}[**]\text{Si}_2\text{S}_4$  are tetrahedrally surrounded by sulfide anions and will be completely isolated from their parent  $\text{Hg}^{2+}$  kernels . As such they would be unassociated , free electrons trapped in the voluminous void spaces in the lattice , suspended in their centers by a tetrahedral coordination to the sulfide electron pairs (Figure 5 , p. [39](#)) .

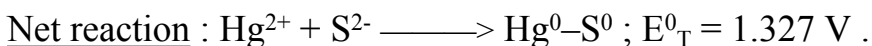
The question immediately arises : wouldn’t the location of a pair of electrons in a cation vacancy be very energetically destabilizing to the system , and indeed even prevent its formation in the reaction ?

This problem is compounded in the case of trying to form a mercury electride , since the usual stabilization energy expected from the dissipation of the point source energy of highly reactive metal atoms into the host structure will be absent with it . Mercury is usually considered as a base metal in commercial and industrial circles , but in redox terms it’s actually a Noble Metal whose zerovalent state is more thermodynamically favorable than either of its univalent or divalent states . Its corresponding  $\text{Hg}^{2+}$  cation is a moderately strong oxidizer ( $E^0_{\text{red}} = 0.851 \text{ V}$  at STP versus the SHE) and can be easily reduced to  $\text{Hg}^0$  by many reducing agents . The mercury atoms will therefore energetically resist giving up their  $6s^2$  inert pairs to the host and forming an electride in it .

The **overall** system energy stabilization must be considered . On the

“negative” side (system energy increase) are the Noble Metal nature of the  $\text{Hg}^0$  guest atoms and the location of the popped inert pairs in the host’s cation vacancies . On the “positive” side (system energy decrease) will be the very strong sulfide— $\rightarrow\text{Hg}^{2+}$  coordinate covalent bonds that will be formed in the product . Given the novelty of the proposed  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  system it would be impossible to estimate its overall system energy stabilization at this point . The feasibility of the  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  synthesis could only be determined by attempting it experimentally .

The mercury–sulfur system has a peculiar redox nature that deserves some comment in the context of a synthesis of  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  . Simple redox equations seem to indicate that Hg–S compounds are actually composed of their zerovalent elements :



The large , positive cell potential  $E_{\text{T}}^0$  for the  $\text{S}^{2-} \rightarrow \text{Hg}^{2+}$  charge transfer implies the net redox reaction as written would be thermodynamically spontaneous at STP.

It should be noted that the standard electrode potentials in the above redox equations were derived from measurements in aqueous media or from thermodynamic calculations , and so might not be fully applicable to solid state systems . However , in very general terms  $\text{Hg}^{2+}$  actually is an electrophilic oxidizer and sulfide anion really is a nucleophilic reducer , so certainly some charge will be transferred from the sulfide to the mercury .

Charge transfer also occurs from mercury to sulfur when the two elements are mixed together :

“The union of mercury and sulfur is effected in the most simple way of all by merely rubbing the two substances together . The product is a black , amorphous compound , quite unlike the bright scarlet crystalline mineral cinnabar” (Henderson and Fernelius , 1935 , [29](#) , their p. 58) .

Presumably when the black, amorphous Hg–S mixture is annealed at a higher temperature it crystallizes into the black  $\beta$ -HgS (metacinnabar), which is known to have the cubic zinc blende structure. Very likely  $\beta$ -HgS is a three-dimensional charge transfer compound in which the valence state of the mercury is intermediate between 0 and  $2+$ , and that of the sulfur has the corresponding value, but negative in sign.

A similar situation could occur in the hypothetical  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  electride. That is, the electrophilic  $\text{Hg}^{2+}$  cations would draw a small amount of negative charge from each of the surrounding four sulfide anions. The sulfide electron pairs would still be coordinating the free electron pairs in the cation vacancies (Figure 5, p. 39), but the sulfides' charge density will have shrunk somewhat, having been partially diverted to the  $\text{Hg}^{2+}$  cations. This “charge transfer mechanism” could help to reduce the energy destabilization caused by the unfavorable residence of the free electron pairs in the cation vacancies.

Three possible locations of the mercury inert pair in  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  are shown in Figure 6, p. 40. In two cases, A and C, the sulfide anion electron pairs ( $3s^2 3p^6$ ) tetrahedrally coordinate the  $\text{Hg}^{2+}$  cations, occupying the latter's  $6s$  and  $6p_{x,y,z}$  orbitals (either native, or with a tetrahedral  $sp^3$  hybridization). Mercury's  $6s^2$  inert pair will have been relocated by the coordination: in the hoped-for case C they will have been “popped” into the voluminous cation vacancies set aside for them. That could result in  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  being a high temperature superconductor.

In case A they will have been promoted into mercury's vacant  $7s,p$  frontier orbitals, resulting in  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  being a conventional metallic solid. This would be energetically feasible because the  $6s,p \rightarrow 7s,p$  energy gap is quite narrow and is easily crossed by reacting species. The free electron pairs would be physically in the very confining interatomic voids, and would still be associated with their parent  $\text{Hg}^{2+}$  kernels.

In case B, however, the inert pair remain  $6s$  in nature, spherically localized around its respective  $\text{Hg}^{2+}$  kernels. No amount of applied pressure can force it either into the  $7s,p$  frontier orbitals or into the cation vacancies. The sulfide electron pairs are still coordinating the  $\text{Hg}^{2+}$  tetrahedrally, but are now using the **outer**  $p^3$  tetrahedral orbitals instead

of the inner  $sp^3$  ones . This electronic form of  $Hg^{2+}[\ast\ast]Si_2S_4$  is predicted to be a non-metallic insulator , clearly not the one we're interested in !

Mercury atoms have been inserted into various sulfide host lattices . Ong and co-workers (1992 , [30](#)) studied the intercalation of mercury in titanium(IV) sulfide , a lustrous , golden metallic solid having the hexagonal cadmium iodide layered structure :

“Triply distilled Hg (< 5 ppm foreign metals) and  $TiS_2$  were loaded into quartz ampoules in a dry box , evacuated to  $< 10^{-4}$  Torr at  $-196\text{ }^\circ\text{C}$  , and flame sealed . The gradual uptake of Hg by the host is apparent at ambient temperature . Samples were homogenized by annealing for 2 days at  $320\text{ }^\circ\text{C}$  , followed by slow cooling to ambient temperature” ([30](#) , their p. 14) .

A half dozen samples of  $Hg^0_xTiS_2$  , with  $x = 0.27-1.29$  , were prepared . In the latter material ,  $Hg^0_{1.29}TiS_2$  , the host  $TiS_2$  interlayer spaces were completely saturated with mercury atoms . The mercury was only weakly bonded to the sulfur atoms :

“TGA of  $Hg_xTiS_2$  shows that Hg begins to slowly deintercalate at about  $170\text{ }^\circ\text{C}$  , and substantial deintercalation occurs only above  $250\text{ }^\circ\text{C}$  and is complete at  $330\text{ }^\circ\text{C}$  .....” ([30](#) , their p. 14) .

From various considerations the researchers concluded ,

“The above observations indicate there is essentially no or very little charge transfer associated with the intercalation of Hg into  $TiS_2$  . A small amount of covalent electron exchange is also possible based on these studies . Hence , we conclude that the primary driving force for Hg– $TiS_2$  intercalation is not the redox reaction of individual guest species with the host , as has been generally assumed for metal–TMD intercalation” ([30](#) , their p. 15 ; TMD = Transition metal dichalcogenide) .

Ong and co-workers annealed their mercury intercalate at  $320\text{ }^\circ\text{C}$  under some pressure in a quartz ampoule . This moderate temperature–pressure treatment apparently was insufficient to bond the mercury guest atoms to the  $TiS_2$  host's sulfur atoms . In the proposed reaction of  $Hg^0$  and  $TiS_2$  the reagents will have to be reacted in a press under **high** pressure and **high**

temperature (HP–HT) conditions in order to permanently bond the Hg and S atoms together and crystallize the product into a zinc blende or wurtzite structure .

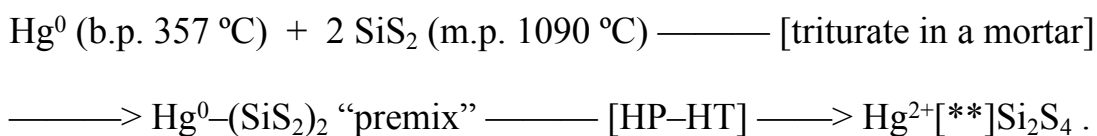
DiSalvo and co-workers (1973 , [31](#)) studied the intercalation of numerous post-Transition metal elements , including mercury , into a tantalum disulfide host lattice . Mercury was readily intercalated into  $\text{TaS}_2$  from the vapor phase at  $200\text{ }^\circ\text{C}$  , forming a stoichiometric 1 : 1 adduct ,  $\text{Hg}_{1.0}\text{TaS}_2$  , in which the mercury atoms were packed into the interlayer void spaces , as in  $\text{TiS}_2$  . The adduct decomposed at  $400\text{ }^\circ\text{C}$  . X-ray diffraction analysis showed that  $\text{Hg}_{1.0}\text{TaS}_2$  had a hexagonal structure similar to the host  $\text{TaS}_2$  . It was a metallic solid , which becomes superconducting at  $T_c = 2.1\text{ K}$  .

The French researchers Padiou , Bideau , and Troadec (1980 , [32](#)) investigated the insertion of one equivalent of copper metal into two equivalents of titanium(IV) sulfide . They obtained the copper(0) adduct  $\text{CuTi}_2\text{S}_4$  , which was a metallic solid with the normal **spinel** crystal structure . The Cu atoms were tetrahedrally coordinated by the sulfide anions in the A sites of the lattice . Since Ti(IV) strongly prefers an octahedral – not tetrahedral – coordination by sulfur , the two Ti(IV) atoms occupied the octahedral B sites in the spinel . Very likely the copper atoms were coordinated as  $\text{Cu}^{1+}$  cations , with their  $4s^1$  valence electrons promoted into the vacant  $5s,p$  frontier orbitals (physically in the interatomic voids) . These latter orbitals , with the promoted electrons , formed the metallic bond–conduction band in the material .

This last example from the research literature suggests that if one equivalent of copper metal powder was combined with two equivalents of silicon(IV) sulfide host , and the mixture was reacted under HP–HT conditions in a press , a zinc blende–wurtzite adduct ,  $\text{Cu}^{1+}[\text{*}]\text{Si}_2\text{S}_4$  , might be obtained in which all the components have a tetrahedral coordination to the others . In this case silicon(IV) always has a tetrahedral coordination with sulfur , even at moderately high pressures (60–65 Kbar , Prewitt and Young , 1965 , [33](#)) . A zinc blende–wurtzite having the critical cation vacancies can thus be preferentially formed instead of an undesirable spinel , which lacks them .



Let's prepare a sample of  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  in a "thought experiment". The obvious route would be to mix one equivalent of  $\text{Hg}^0$  with two equivalents of  $\text{SiS}_2$ , then anneal the mixture under HP-HT conditions to irreversibly bind all the atomic components together with strong Si-S covalent and Hg-S coordinate covalent bonds.  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  should crystallize into the desired zinc blende-wurtzite containing stoichiometric numbers of cation vacancies (which hopefully contain the pairs of free, unassociated electrons):



The host structure silicon(IV) sulfide is a silicon-sulfur polymer comprised of long Si-S chains [34](#), and physically having a remarkable fibrous morphology with large interchain spaces that could readily host the added mercury atoms. One equivalent of mercury would be gently triturated in a mortar with two equivalents of silicon(IV) sulfide; this would likely form a black, amorphous premix material with weak Hg-S bonds, as in the  $\text{Hg}_x\text{TiS}_2$  discussed above. This premix would be annealed in a press under HP-HT conditions to crystallize it into the zinc blende-wurtzite structure. If only a low pressure is used, the non-metallic insulator  $\text{Hg}^0[\ ]\text{Si}_2\text{S}_4$ , with mercury's  $6s^2$  inert pairs still spherically distributed around the  $\text{Hg}^{2+}$  kernel, might be formed. At higher pressures the "ordinary metallic" compound  $\text{Hg}^{2+}[\ ]\text{Si}_2\text{S}_4$  ( $\text{**}$ )<sub>7s,p</sub>, or the desired material,  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$ , would preferably be produced.

Silicon disulfide, while commercially available, readily hydrolyses in humid air to the point where it is said to "smell like rotten eggs" [34](#) from the  $\text{H}_2\text{S}$  evolving from its surface. It might be more convenient to prepare it *in situ* in the reaction mixture from its component elements, as described, for example, by Yamamoto and Ikeda (1997, [35](#)). Prewitt and Young ([33](#)) also prepared  $\text{SiS}_2$  directly from its elements in HP-HT conditions. Another convenient preparation of  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$ , using readily available and inexpensive elements, might proceed as follows:

1.  $\text{Hg}^0 + \text{S}^0 \xrightarrow{\text{triturate in a mortar}} \text{Hg}^0\text{-S}^0$ , “black ,  
amorphous” [29](#) , not isolated pure ;
2.  $\text{Hg}^0\text{-S}^0 + 2 \text{Si}^0$  (fine powder) +  $3 \text{S}^0 \xrightarrow{\text{triturate}} \text{mix}$  ;
3. mix  $\xrightarrow{\text{[HP-HT, high pressure]}} \text{Hg}^{2+[\ast\ast]}\text{Si}_2\text{S}_4$  .

The volatile liquid mercury might be more conveniently used in this reaction by first “fixing” it in a solid form with an equivalent of sulfur (as flowers of sulfur powder) . The remaining silicon and sulfur components are then blended into the  $\text{Hg}^0\text{-S}^0$  premix , and the thoroughly ground mixture is subjected to HP-HT conditions in a suitable press .

The other two members of the IIB/12 family of elements , zinc and cadmium , might also be used in similar reactions to prepare the analogue zinc blende-wurtzites ,  $\text{Zn}^{2+[\ast\ast]}\text{Si}_2\text{S}_4$  and  $\text{Cd}^{2+[\ast\ast]}\text{Si}_2\text{S}_4$  . ZnS and CdS are well-known compounds having both the zinc blende and wurtzite crystal structures . Zinc and cadmium are base metals and reducing agents . Zinc is a moderately strong reducer with  $E^0_{\text{ox}} = 0.7618 \text{ V}$  ; cadmium is somewhat less so with  $E^0_{\text{ox}} = 0.403 \text{ V}$  . They should thus form electriles in the  $\text{SiS}_2$  host lattice more readily than mercury :

$\text{ZnS}$  (m.p.  $1700 \text{ }^\circ\text{C}$ ) +  $2 \text{Si}^0$  (m.p.  $1414 \text{ }^\circ\text{C}$ ) +  $3 \text{S}^0$  (m.p.  $115 \text{ }^\circ\text{C}$  ,

b.p.  $445 \text{ }^\circ\text{C}$ )  $\xrightarrow{\text{[HP-HT]}} \text{Zn}^{2+[\ast\ast]}\text{Si}_2\text{S}_4$  ;

$\text{CdS}$  (subl.  $980 \text{ }^\circ\text{C}$ ) +  $2 \text{Si}^0 + 3 \text{S}^0 \xrightarrow{\text{[HP-HT]}}$

$\text{Cd}^{2+[\ast\ast]}\text{Si}_2\text{S}_4$  .

**Caution** : the reaction of zinc powder with flowers of sulfur is an extremely exothermic reaction [36](#) like Thermit and should not be attempted for the above reaction .

Because zinc is a base metal and a moderately strong reducer it might form the corresponding electrile in silica ,  $\text{Zn}^{2+[\ast\ast]}\text{Si}_2\text{O}_4$  . Silica , as its most common naturally-occurring polymorph  $\alpha$ -quartz [37](#) , could potentially act

as a host lattice for many elementary atoms , both metallic and non-metallic [38](#) . Alpha-quartz has channels of huge void spaces between the chains of  $\text{SiO}_4$  polyhedra [39](#) into which various type of atoms could readily diffuse . The more reactive , electropositive elements like zinc could then chemically react with the electronegative oxygen linking atoms to form M–O oxides *in situ* . If a stoichiometric ratio of  $1 \text{ Zn}^0 : 2 \text{ SiO}_2$  is carefully observed , the compound resulting from a HP–HT synthesis could be a double wurtzite (note that ZnO has the wurtzite crystal structure only , so its derivative  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  probably would , too) :

$\text{Zn}^0$  (m.p. 420 °C , b.p. 907 °C) + 2  $\text{SiO}_2$  (m.p. 1722 °C)

———— [HP–HT] —————>  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  .

The thermodynamic balance in  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  looks quite favorable , certainly much better than in  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  . Since the zinc atoms are natural reducers , their point source energy will be dispersed over the entire lattice of  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  , which will itself become mildly reducing in nature . That will provide some energy stabilization , unlike the case with the Noble metal mercury . Second , zinc oxide has a very high melting point , 1974 °C , indicating in a very simple manner that its Zn–O chemical bonds , which are probably coordinate covalent , are immensely strong . This will also be energetically very favorable for the electride formation .

Zinc has several other differences with mercury in the synthesis of these proposed zinc blende–wurtzites :

\* It has no redox interaction with oxygen , which unlike the chemically reducing sulfide anion , has no reducing nature whatsoever . The mildly electrophilic zinc cation will slightly polarize the coordinating oxygen linking atoms , slightly reducing their electronegative charge . Because the Zn–O bonding in the hypothetical  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  is coordinate covalent , the oxygen atoms won't be anions with full negative charges .

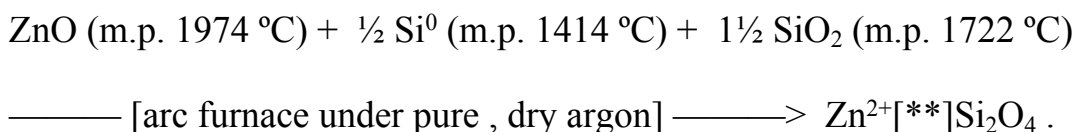
\* The crystal ionic radius of  $\text{Zn}^{2+}$  (CN = 4 , ie. tetrahedral , per Shannon and Prewitt) is  $r = 0.60 \text{ \AA}$  , compared to that of  $\text{Hg}^{2+}$  , which is much

larger , at  $r = 0.96 \text{ \AA}$  ,  $\text{CN} = 4$  . Zinc will therefore fit more comfortably in a host lattice with Si(IV) , which has  $r = 0.26 \text{ \AA}$  .

\* Zinc and silica are widely abundant in Nature and as commercial commodities they are available in huge quantities (Figure 7 , p. [41](#)) . Mercury would be economically impractical for any large volume industrial applications .

\* Again with a future wide-scale development in mind , zinc is a relatively non-toxic , innocuous element (familiar in common use as the rust-proof coating on galvanized steel) , while mercury is a toxic heavy metal whose use in many existing applications (eg. fluorescent lighting) is gradually being phased out , and is being replaced by less toxic alternatives .

Consider another possible synthesis of  $\text{Zn}^{2+[\ast\ast]}\text{Si}_2\text{O}_4$  :



In the above equation the free electron pair would be derived from the elementary silicon component . Since silicon has four available valence shell electrons , half of an equivalent of it would provide the required two free electrons for the electride , rather than from the zinc . The required quantity of silica must then be adjusted downward in order to have the correct overall amount of silicon in the reaction mixture .

The highly refractive nature of the three reagents suggests an alternate synthesis method for the electride , that of fusing a pellet of the reaction mixture in an **arc furnace** under a protective atmosphere of pure , dry argon . Such a technique has been adapted for the preparation of various refractory inorganic compounds , such as the synthetic metal niobium monoxide [40](#) .

While mercury atoms might diffuse into the interpolyhedral void spaces of  $\alpha$ -quartz , the oxygen linking atoms – lacking the nucleophilic strength of sulfide anions – would be unable to “pop” mercury’s  $6s^2$  inert pairs into the void spaces and thereby form an electride in the silica host .

Cadmium might also be unsuitable as the guest atoms in an  $\alpha$ -quartz host .  $\text{Cd}^{2+}$  cations seem to prefer an octahedral , rather than a tetrahedral coordination when bonded to oxygen , at least in ionic compounds such as cadmium oxide , which has the rocksalt structure .

Lithium cation is almost the same size ( $r = 0.59 \text{ \AA}$  ,  $\text{CN} = 4$ ) as  $\text{Zn}^{2+}$  and similarly prefers a tetrahedral coordination when bonded to oxygen anions and linking atoms (eg. as in  $\text{Li}_2\text{O}$  , with the antifluorite structure) . Synthesis of the hypothetical zinc blende–wurtzite  $\text{Li}^{1+[*]}\text{Si}_2\text{O}_4$  should be both feasible and very important from a theoretical point of view :



Lithium metasilicate , which is commercially available as a reasonably pure reagent chemical , could serve as the source for both the lithium cation and for some of the silica . One-quarter equivalent of silicon could provide the free electron in the cation vacancy .

$\text{Li}^{1+[*]}\text{Si}_2\text{O}_4$  would be composed of alternating layers of  $\text{SiO}_2$  and of  $\text{Li}_2\text{O}$  and tetrahedral cation vacancies having a singlet free electron [\*] . Would the free electrons be completely unassociated with the lattice and be mobile in it under an applied p.d. in a resistance-free manner ; that is , would  $\text{Li}^{1+[*]}\text{Si}_2\text{O}_4$  be a high temperature superconductor , even though singlet free electrons rather than electron pairs are the charge and energy carriers ? Or would it become superconducting only near Absolute Zero , if at all ? Might the free electrons in the cation vacancies actually be **polarons** , making  $\text{Li}^{1+[*]}\text{Si}_2\text{O}_4$  a “hopping semiconductor” like  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4e^-]$  ? It would be a most interesting [41](#) experiment !

The possibility of synthesizing the analogous zinc blende–wurtzite  $\text{Cu}^{1+[*]}\text{Si}_2\text{S}_4$  was mentioned above on page 16 . It would similarly be useful and instructive to study .  $\text{Cu}^{1+}$  usually prefers a tetrahedral coordination by sulfide anions , but uniquely favors a linear coordination

by oxides (ionic bonding) and oxygen linking atoms (covalent bonding) . While some sort of compound having the formula  $\text{CuSi}_2\text{O}_4$  might be synthesized , it certainly wouldn't be a zinc blende–wurtzite .

## Organic Electrideres : Polarons and Bipolarons

As mentioned above on page 5 , Prof. Dye and his co-workers have carried out , over the recent couple of decades , much groundbreaking research in the synthesis and study of organic electrideres [12](#) . Various ligands formed strong coordinate covalent complexes with the Alkali metal atoms , energetically assisting them to dissociate into the corresponding cation and free electron . The latter is trapped in cavities and channels in the crystalline Alkali metal electrideres .

In searching for molecules which might act as “containers” for the free electrons , in order to help protect them from external oxidizers like water molecules and atmospheric oxygen , an idea emerged to use **betaines** as the complexing agents with the electrideres in anhydrous liquid ammonia (Figure 8 , p. [42](#)) . A bis-betaine could act as a sort of chelating agent , binding the Alkali or Alkaline Earth metal cation at one end , while enclosing the singlet free electron or pair of electrons within its ring .

On further consideration the the metal cation–carboxylate part of the complex was deemed expendable and was removed from it . A second set of organic electrideres was designed having onium and bis-onium cationic centers to which were respectively associated single and pairs of free electrons (Figure 9 , p. [43](#)) . It was initially hoped that these organic electrideres with the pairs of free electrons might be high temperature superconductors , but a review of the electrideres research literature , especially that cited above by Dye [6](#) and Hosono [20](#) , strongly implied that the electron pairs in these latter proposed compounds would almost certainly be bipolarons [42](#) (and the singlet electrons in them would be polarons) . That is , they would be acting as the anions and dianions in the electrideres “salt”, exactly as the free electrons in electrideres have long been portrayed . For example , the electron pairs in the proposed organic electrideres in Figure 9 , p. [43](#) , would resemble , say , sulfate anions , and

would be bonded inside their parent organic molecule containers by strong ionic bonds , as in the common salt sodium sulfate . Far from being high temperature superconductors , these organic electrides would almost certainly be the complete opposite of them : non-metallic electrical insulators , or at best , hopping semiconductors like Hosono's inorganic electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4e^-]$  .

When melted , salts like the common NaCl become ionic conductors . In the organic electrides sketched in Figure 9 , p. [43](#) , the pairs of free electrons are very powerful reducing agents . They are unassociated orbitally with any of the organic molecule's carbon and nitrogen atoms , which all have completed valence shells with electron octets . Carbon and nitrogen are 2s,p elements , whose 3s,p frontier orbitals are at far too high an energy level to be accessible to the thermally excited free electron pairs . The C–C and C–N antibonding molecular orbitals ( $\sigma^*$  ABMOs) might possibly be energetically accessible to them when provided with enough thermal energy . However , when the electron pairs enter these ABMOs they cancel out entire C–C and C–N covalent bonds . If this process happened within a few milliseconds , the entire molecule would disintegrate into small gas molecules . In plain language the electride would **explode** [43](#) . Strongly or rapidly heating it would be highly unadvisable !

The betaine electrides should therefore be considered only as polaron and bipolaron organic molecules , and not as high temperature superconductor candidates . They would be an entirely new class of electronic materials , undoubtedly fascinating in their own right and deserving of study and possible development for practical applications .

## Concluding Remarks

The concept of isolating free electrons from their parent atomic kernels in a host lattice as in the electrides , in the design of new high temperature superconductors , may not be such a new idea after all . For example , in the superconducting cuprates such as YBCO (idealized empirical formula  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ) the  $\text{Cu}^{2+} 3d^9$  valence electrons are the ones forming the

Cooper pairs in the superconducting state . They are isolated from their  $\text{Cu}^{3+}$  parent kernels by the oxide anions coordinating them (four-coordinate square planar in the  $\text{Ba}_2\text{Cu}_2\text{O}_4$  layers , and five-coordinate square pyramid in the  $\text{YCuO}_3$  layers) . YBCO could reasonably be considered as a  $\text{Cu}^{2+}$  electrone in the Y–Ba–O host lattice .

The layered structure of YBCO also provides substantial interlayer void space in which the Cooper pairs can flow through the lattice under an applied potential difference . The mixed-valent nature of YBCO with  $\text{Cu}^{2+}$ – $\text{Cu}^{3+}$  (it's a Robin-Day Class II mixed-valent compound) causes an ultra fast resonance of the Cu  $3d^9$  electrons between the Cu cations via superexchange through the oxide anions , making YBCO a metallic solid . As pointed out on page 3 , the strongly antiferromagnetic [4](#) copper(II) oxide lattice helps to organize the spins of the now-itinerant  $3d^9$  electrons into an antiparallel régime . All these factors promote the condensation of the  $\text{Cu}^{2+}$   $3d^9$  electrons into Cooper pairs at an unusually high transition temperature (93 K) .

The oxide anions coordinating around the copper cations help to isolate the  $3d^9$  electrons from their Cu kernels , permitting the former to become dissociated from them . The isolation must be essentially perfect below  $T_c$  , because Cooper pairs rather than bipolarons are formed in the YBCO lattice . In the examples of  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  and  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  we are hoping that the free electrons will similarly be perfectly isolated from their respective  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  parent kernels . However , unlike with YBCO where we are trying to couple together singlet electrons , in the proposed zinc blende–wurtzites the free electron pairs are already pre-formed in their cation vacancies as a consequence of the chemical synthesis , and they should be stable in the lattice at all temperatures at which the host structure is stable (which could be well above room temperature) .

The hypothesis which forms the theme of this essay originated from the contemplation of superconductivity in mercury frozen in liquid helium at 4 K . The precise nature of this phenomenon remains as mysterious as ever . If all the mercury atoms'  $6s^2$  inert pairs “pop off” their respective  $\text{Hg}^{2+}$  parent kernels and drift into the interatomic void spaces where they become unassociated Cooper pairs , then the underlying atomic lattice



must , by default , become strongly cationic in coulombic charge . That being the case , why don't the "popped" inert pairs become bipolarons instead of Cooper pairs ? A simple answer could be that they **remain** in the metallic bond–conduction band orbitals , but are condensed into spin pairs having the electronically stable  $1s^2$  configuration , like helium .

Undoubtedly the polaron–bipolaron problem will continue to play a central role in the future design and synthesis of high temperature superconductors . The ingenuity and creativity of solid state chemists will be increasingly called on in addressing this critical issue . The collaboration of condensed matter physicists with their chemist colleagues will be essential for progress in superconductivity research . Five decades ago an imaginative and innovative physicist at Stanford University , William A. Little (who aroused some controversy and excitement in the field by his proposal of room temperature superconductors based on conductive organic polymers [44](#)) , wrote in a Symposium report (1970) ,

“In conclusion I would like to stress that in this field there is a desperate need for an interdisciplinary approach . I think physicists on the whole *understand* a great deal but they *know* very little . On the other hand the chemist with his vast experience of reactions , compounds , conditions , etc. *knows* a great deal but .... , well , perhaps I will not push the contrast further but will conclude by saying that we need each other” ([45](#) , p. 26) .

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## References and **Notes**

- \* You can click on the reference number (left hand side of the page) to return to the section of text in which the citation first appeared (or use the navigation buttons on your PDF reader , of course) .
- \* The external links (Internet URLs) were accessed on April 17<sup>th</sup>, 2016 , and all of them were confirmed to be active and fully functional .
- \* This presentation is only an outline , or overview , of the topic of high temperature superconductors designed according to the “unassociated , free electrons” hypothesis introduced at the beginning of this essay . For a fuller , more detailed discussion of the subject , interested readers are invited to peruse the following web pages from Chemexplore :

“A New Picture of Superconductivity : Lightning Bolt [Electrons](#) in a Crystal” ;

“[Perovskites](#) Designed as Drude Metals and Ambient Superconductors” ;

“[Rocksalts](#) Designed as Super-electrides , Drude Metals , and as Possible High Temperature Superconductors” ;

“[Chromium](#) as the Guest Atom in Super-electride Drude Metals” ;

“[Lead](#) , Tin , and Bismuth as the Guest Atoms in Super-electride Drude Metals” ;

“[Betaines](#) and Electrides : From Sugar Beets and Baby Shampoo to Superconductors” ; and ,

“Drude Electron Materials Having [Rutile](#) and Layered Structures” .

In these web pages the new high temperature superconductor candidates such as  $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$  and  $\text{Zn}^{2+}[\text{**}]\text{Si}_2\text{O}_4$  were termed **Drude electron materials** . The entirely free , unassociated electrons were named “Drude electrons” in honor of , and homage to , the German physicist [Paul Drude](#) (1863-1906 , another [web page](#)) who in 1900 introduced the first electron theory of metals . In this model the mobile conduction electrons in metals were treated as an inert monoatomic gas , rather like helium atoms . The introduction of atomic orbitals by Bohr in 1913 , and in particular the quantum mechanical treatment of conduction electrons by Fermi and Dirac in 1926 , modernized Drude’s simpler picture of the electrons .

[1](#) The following two articles describe , at a basic “undergraduate” level , the quantum behaviour of conduction electrons in metals :

A.R. Mackintosh , “The Fermi Surface of Metals”, Scientific American [209](#) (1) , pp. 110-120 (July , 1963) [DOI](#) ; and ,

W.J. Moore , Seven Solid States , An Introduction to the Chemistry and Physics of Solids , W.A. Benjamin , New York , 1967 ; Ch. 2 , “Gold” , pp. 41-72 . This is my favourite solid state chemistry textbook , now out of print . If your Science Library doesn’t have a copy , you might be able to buy an inexpensive second-hand copy from [ABE](#) , the Advanced Book Exchange .

[2](#) A.B. Ellis et al. , Teaching General Chemistry , A Materials Science Companion , American Chemical Society , Washington , D.C. , 1993 ; pp. 191-192 (example of sodium metal) .

[3](#) C.P. Poole Jr. , H.A. Farach , and R.J. Creswick , Superconductivity , Academic Press , San Diego , CA , 1995 ; Table 3.1 , “Properties of the Superconducting Elements” , pp. 60-61 . The twenty-nine elements listed are superconducting at ambient pressure (one atmosphere) ; several more elements become superconducting near Absolute Zero under extremely high pressures .

[4](#) N.A. Cade and W. Yeung , “Antiferromagnetically Induced Electron Pairing” , Physica C : Superconductivity [152](#) (5) , pp. 389-396 (1988) [DOI](#) ; Chemexplore web page , “[Antiferromagnetic](#) Induction in High Temperature Superconductors” ; idem. , “New [Layered](#) Compounds for High Temperature Superconductivity” ; idem. , “High Temperature Superconductor Candidates Based on [Modified](#)  $\text{La}_2\text{CuO}_4$  and  $\text{La}_2\text{NiO}_4$ ” ; Chemexplore graphic : “The Antiferromagnetic (AFM) Induction Model” , [GIF image](#) , 77 KB .

[5](#) The term “crystal orbital” has been used in two excellent solid state chemistry textbooks : P.A. Cox , The Electronic Structure and Chemistry of Solids , Oxford University Press , Oxford , UK , 1987 ; Ch. 4 , pp. 79-133 ; and R. Hoffmann , Solids and Surfaces , A Chemist’s View of Bonding in Extended Structures , VCH Publishers , New York , 1988 ; pp. 43-55 .

- [6](#) J.L. Dye , “Electrides : Early Examples of Quantum Confinement”, Acc. Chem. Res. **42** (10) , pp. 1564-1572 (2009) [DOI](#) ; p. 1566 .
- [7](#) P.P. Edwards , “The Electronic Properties of Metal Solutions in Liquid Ammonia and Related Solvents”, Adv. Inorg. Chem. Radiochem. **25** , pp. 135-185 , H.J. Emeléus and H.G. Sharpe (eds.), Academic Press , New York (1982) [DOI](#) ; J.L. Dye , “Electrides , Negatively Charged Metal Ions , and Related Phenomena”, Prog. Inorg. Chem. **32** , pp. 327-441, S.J. Lippard (ed.) , John Wiley , New York (1984) [DOI](#) ; J.L. Dye and M.G. DeBacker , “Physical and Chemical Properties of Alkalides and Electrides”, Ann. Rev. Phys. Chem. **38** , pp. 271-301 (1987) [DOI](#) ; M.J. Wagner and J.L. Dye , “Alkalides , Electrides , and Expanded Metals”, Ann. Rev. Mater. Sci. **23** , pp. 223-253 (1993) [DOI](#) .
- [8](#) J.L. Dye , “Electrides : Ionic Salts with Electrons as the Anions”, Science **247** (4943) , pp. 663-668 (1990) [DOI](#) ; *ibid.* , “Electrons as Anions”, Science **301** (5633) , pp. 607-608 (2003) [DOI](#) .
- [9](#) J.L. Dye , “The Solvated Electron”, Scientific American **216** (2) , pp. 76-83 (February , 1967) [DOI](#) ; sketches on p. 78 .
- [10](#) M.C.R. Symons , “Nature of Metal Solutions”, Quart. Rev. **13** (2) , pp. 99-115 (1959) [DOI](#) ; mentioned on p. 99 .
- [11](#) J.C. Warf and W.L. Korst , “Solutions of Europium and Ytterbium Metals in Liquid Ammonia”, J. Phys. Chem. **60** (11) , pp. 1590-1591 (1956) [DOI](#) .
- [12](#) J.L. Dye , ref. 6 above , pp. 1567-1569 ; M.Y. Redko , J.E. Jackson , R.H. Huang , and J.L. Dye , “Design and Synthesis of a Thermally Stable Organic Electride”, J. Am. Chem. Soc. **127** (35) , pp. 12416-12422 (2005) [DOI](#) ; S.K. Ritter , “Mission Accomplished : A Stable Electride”, Chem. Eng. News **83** (41) , p. 45 (2005) [DOI](#) .
- [13](#) P.P. Edwards , P.A. Anderson , and J.M. Thomas , “Dissolved Alkali Metals in Zeolites”, Acc. Chem. Res. **29** (1) , pp. 23-29 (1996) [DOI](#) .

- [14](#) H. Buchhammagari , Y. Toda , M. Hirano , H. Hosono , D. Takeuchi , and K. Osakada , “Room Temperature-Stable Electride as a Synthetic Organic Reagent : Application to Pinacol Coupling Reaction in Aqueous Media”, *Org. Lett.* **9** (21) , pp. 4287-4289 (2007) [DOI](#) ; S.W. Kim , T. Shimoyama , and H. Hosono , “Solvated Electrons in High-Temperature Melts and Glasses of the Room-Temperature Stable Electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4e^-]$ ”, *Science* **333** (6038) , pp. 71-74 (2011) [DOI](#) ; S.W. Kim , S. Matsuishi , T. Nomura , Y. Kubota , M. Takata , K. Hayashi , T. Kamiya , M. Hirano , and H. Hosono , “Metallic State in a Lime-Alumina Compound with Nanoporous Structure”, *Nano Lett.* **7** (5) , pp. 1138-1143 (2007) [DOI](#) .
- [15](#) E.T. Keve and A.C. Skapski , “ $\text{Ca}_2\text{N}$  : A Nitride with a Layer Structure”, *Chem. Commun.* **1966** (22) , pp. 829-830 [DOI](#) .
- [16](#) D.H. Gregory , A. Bowman , C.F. Baker , and D.P. Weston , “Dicalcium Nitride ,  $\text{Ca}_2\text{N}$  – A 2D “Excess Electron” Compound ; Synthetic Routes and Crystal Chemistry”, *J. Mater. Chem.* **10** (7) , pp. 1635-1641 (2000) [DOI](#) .
- [17](#) K. Lee , S.W. Kim , Y. Toda , S. Matsuishi , and H. Hosono , “Dicalcium Nitride as a Two-Dimensional Electride with an Anionic Electron Layer”, *Nature* **494** (7437) , pp. 336-341 (2013) [DOI](#) .
- [18](#) A. Walsh and D.O. Scanlon , “Electron Excess in Alkaline Earth Subnitrides : 2D Electron Gas or 3D Electride ?”, *J. Mater. Chem. C* **1** (22) , pp. 3525-3528 (2013) [DOI](#) ; open access article : [HTML](#) or [PDF](#) (349 KB) .
- [19](#) M.B. Robin and P. Day , “Mixed Valence Chemistry – A Survey and Classification”, *Adv. Inorg. Chem. Radiochem.* **10** , pp. 247-422 , H.J. Emeléus and A.G. Sharpe (eds.) , Academic Press , New York (1967) [DOI](#) .
- [20](#) S. Matsuishi , Y. Toda , M. Miyakawa , K. Hayashi , T. Kamiya , M. Hirano , I. Tanaka , and H. Hosono , “High Density Electrons in a Nanoporous Single Crystal :  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4e^-]$ ”, *Science* **301** (5633) , pp. 626-629 (2003) [DOI](#) .

[21](#) A more atom efficient , cleaner (no solid by-products) , and generally simpler method of synthesizing the zeolite electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4\text{e}^-]$  might be by **electron doping** the non-metallic precursor  $\text{Ca}_{22}\text{Al}_{28}\text{O}_{64}$  with calcium metal :



M = Mg , Ca , Sr , Ba , Zn , Cd , Sn , Pb ; possibly also various divalent Transition metal elements such as V, Cr , Mn , Fe , Co , and Ni .

Since calcium metal is rather expensive and its high reactivity makes it a nuisance to handle , an improved procedure might be to use **aluminum** metal as the electron doping agent . Aluminum is widely available as an inexpensive chemical reagent in a pure , granular form (**caution** : very finely divided metal powders can be **pyrophoric** !) which is easy to handle in the laboratory and weigh out .  $\text{Al}^0$  can provide its three valence electrons to the reaction mix . As four free electrons are required per equivalent of electride ,  $4/3$  equivalent of  $\text{Al}^0$  must be used in the formulation . The  $4/3$  equivalent of  $\text{Al}^0$  must be deducted from the  $\text{Al}_2\text{O}_3$  contribution to the formulation . The “spent”  $\text{Al}^{3+}$  cations will participate in forming the zeolite compound , completing its cage structure :



As indicated in the formulas , suitable divalent elements other than calcium could also be studied in the synthesis of  $[\text{M}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} [4\text{e}^-]$  analogues . There’s still plenty of interesting chemistry to investigate with this class of zeolite electrides !

[22](#) Wikipedia [web page](#) (in German) , “Robert Wichard Pohl” , its ref. 12 .

[23](#) M. Miyakawa , S.W. Kim , M. Hirano , Y. Kohama , H. Kawaji , T. Atake , H. Ikegami , K. Kono , and H. Hosono , “Superconductivity in an Inorganic Electride  $12 \text{CaO} \cdot 7\text{Al}_2\text{O}_3 : e^-$ ”, *J. Am. Chem. Soc.* **129** (23) , pp. 7270-7271 (2007) [DOI](#) . See also S.W. Kim , M. Miyakawa , M. Hirano , Y. Kohama , H. Kawaji , T. Atake , H. Ikegami , K. Kono , and H. Hosono , “Superconducting Transition in Electron-Doped  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ ”, *Mater. Trans.* **49** (8) , pp. 1748-1752 (2008) [DOI](#) ; full [PDF](#) (214 KB) .

[24](#) K. Andres , N.A. Kuebler , and M.B. Robin , “Superconductivity in  $\text{Ag}_2\text{F}$ ”, *J. Phys. Chem. Solids* **27** (11-12) , pp. 1747-1748 (1966) [DOI](#) .

[25](#) E.K.S. Liu and R.J. Lagow , “The Preservation of Metal–Carbon Bonds and Metalloid–Carbon Bonds During Direct Fluorination : A Surprise Even to Fluorine Chemists”, *J. Am. Chem. Soc.* **98** (25) , pp. 8270-8271 (1976) [DOI](#) . Dimethylmercury ,  $\text{H}_3\text{C–Hg–CH}_3$  , was perfluorinated at  $-78$  to  $-90$  °C to bis(trifluoromethyl)mercury in a 6.5% yield .  $\text{F}_3\text{C–Hg–CF}_3$  can be further fluorinated at  $0$  °C and at room temperature to  $\text{CF}_4$  and  $\text{HgF}_2$  . The authors interpret these findings as demonstrating the surprising strength of the Hg–C bonds . However , it should be noted that the fluorine attacked the carbon and hydrogen atoms in dimethylmercury , and **not** the mercury atom . That is , the fluorine failed to oxidize the mercury  $5d^{10}$  electrons , which seem to be deeply embedded in the mercury kernel and inaccessible even to fluorine , the most powerful oxidizer known in chemistry .

[26](#) American Physical Society [web page](#) , “This Month in Physics History , April , 1911 : Onnes Begins Work on Superconductivity”.

[27](#) anon. , Web document , “Thermochromism in the Ionic Conductor ,  $\text{Cu}_2\text{HgI}_4$ ”, University of Massachusetts [PDF](#) , 223 KB .

[28](#) The coordination of all the components of the double zinc blende–wurtzites is tetrahedral . If the coordination of the M atoms in  $\text{AM}_2\text{X}_4$  is octahedral , the compound will likely be a **spinel** , which won't have any cation vacancies :  $\text{A}_{\text{tet}}(\text{M}_{\text{oct}})_2\text{X}_4$  . This is why silicon(IV) , which always has a tetrahedral coordination to other atoms (at least , at ambient and moderate pressures) , will be very useful in the design of new double zinc blende–wurtzites with cation vacancies :  $\text{A}_{\text{tet}}[\ ]_{\text{tet}}(\text{Si}_{\text{tet}})_2(\text{X}_{\text{tet}})_4$  .

[29](#) W.E. Henderson and W.C. Fernelius , A Course in Inorganic Preparations , McGraw-Hill , New York , 1935 ; p. 58 . This useful inorganic chemistry syntheses textbook can be downloaded for free from the [Sciencemadness.org library resources web page \[DJVU , 1396 KB\]](#) . I highly recommend the [Sumatra PDF Reader](#) (freeware , supported by Windows XP and later) , which is a simple , “light” , efficient reader of PDF , DjVu , and ebook formats .

[30](#) E.W. Ong , M.J. McKelvey , G. Ouvrard , and W.S. Glaunsinger , “Mercury Intercalates of Titanium Disulfide : Novel Intercalation Compounds” , Chem. Mater. **4** (1) , pp. 14-17 (1992) [DOI](#) .

[31](#) F.J. Di Salvo et al. , “Metal Intercalation Compounds of TaS<sub>2</sub> : Preparation and Properties” , J. Chem. Phys. **59** (4) , pp. 1922-1929 (1973) [DOI](#) .

[32](#) J. Padiou , D. Bideau , and J.P. Troadec , “Propriétés Magnétiques et Électriques de Thiospinelles Quaternaires” , J. Solid State Chem. **31** (3) , pp. 401-405 (1980) [DOI](#) . See also : N. Soheilnia , K. M. Kleinke , E. Dashjav , H. L. Cuthbert , J. E. Greedan , and H. Kleinke , “Crystal Structure and Physical Properties of a New CuTi<sub>2</sub>S<sub>4</sub> Modification in Comparison to the Thiospinel” , Inorg. Chem. **43** (20) , pp. 6473-6478 (2004) [DOI](#) .

[33](#) C.T. Prewitt and H.S. Young , “Germanium and Silicon Disulfides : Structure and Synthesis” , Science **149** (3683) , pp. 535-537 (1965) [DOI](#) ; Chemexplore graphic , [GIF image](#) , 70 KB .

[34](#) Wikipedia [web page](#) , “Silicon Sulfide” ; Chemexplore graphic , [GIF image](#) , 55 KB .

[35](#) K. Yamamoto and N. Ikeda , “Method of Manufacturing Silicon Sulfide” , U.S. Patent 5843391 , December 1<sup>st</sup>, 1998 [PDF](#) , 292 KB ; Chemexplore graphic , [GIF image](#) , 48 KB .

[36](#) Three impressive YouTube videos showing the highly exothermic zinc–sulfur reaction : a demonstration from the University of Nottingham ,



UK [[MP4](#) , 13,485 KB , runtime 3:10] ; one showing a Zn + S mixture used as a rocket propellant [[MP4](#) , 731 KB , runtime 0:09] ; and one illustrating the fiery combustion of Zn + S [[MP4](#) , 1621 KB , runtime 0:19] . These videos can be saved to a C:\ archive via the [KeepVid](#) website .

[37](#) Wikipedia [web page](#) , “Silicon Dioxide” .

[38](#) Many minerals are colored by inclusions of foreign atoms in their lattices . Well known examples include the ruby ( $\text{Cr}^{3+}$  in an alumina host ; see in Moore’s textbook , ref. 1 above , Ch. 6 , “Ruby” , pp. 163-188) , the sapphire (Fe and Ti in alumina) ; [blue diamonds](#) (boron doped into carbon) ; and [yellow diamonds](#) (nitrogen doped into carbon) . My study of the chemistry of zerovalent compounds formed by the insertion of elements into host lattices originated from noticing an attractive specimen of rose quartz in a mineral shop one day . The card attached to the mineral noted it was colored by the inclusion of gold atoms , which aroused my interest . I wondered if various stoichiometric quantities of gold reagent could be combined with silica , and if so , what the crystal structure and physical and chemical properties of the resultant compounds might be (keeping in mind that gold is a Noble metal and therefore wouldn’t react in a redox manner with the silicon) . What other elementary atoms might be inserted into the lattice of  $\alpha$ -quartz , with its large interpolyhedral void spaces ? Recall that ferrosilicon is used in the [Pidgeon Process](#) for the [production of magnesium metal](#) from magnesite and dolomite . Magnesium is a powerful reducing agent ( $E_{\text{ox}} = 2.372 \text{ V}$ ) . This suggests that a wide variety of metal elements could be hosted by silica . Numerous metalloids and non-metals (pnictides , chalcogenides , and maybe even halides) might similarly be combined with silica in stoichiometric quantities to prepare many new zerovalent compounds having interesting and potentially useful electronic properties .

[39](#) [Web page](#) “S097-alpha-quartz” (polyhedral crystal model) ; [web page](#) “ $\text{SiO}_2$  (alpha)” (ball-and-stick crystal model) .

[40](#) T.B. Reed and E.R. Pollard , “Niobium Monoxide” , [Inorg. Synth.](#) [14](#) , A. Wold and J.K. Ruff (eds.) , McGraw-Hill , New York , 1973 ; pp. 131-134 [DOI](#) ; [PDF](#) (7530 KB for the entire vol. 14) ; reprinted in [Inorg. Synth.](#) [30](#) , [Nonmolecular Solids](#) , D.W. Murphy and L.V. Interrante

(eds.) , John Wiley , New York , 1995 ; pp. 108-110 [DOI](#) ; [PDF](#) (11,593 KB for the entire vol. 30) . A review of the arc furnace method of synthesis involving refractory materials : T.B. Reed , “Arc Techniques for Materials Research” , Mater. Res. Bull. 2 (3) , pp. 349-367 (1967) [DOI](#) . A home-made arc furnace is described by [Theodore Gray](#) , “Melting the Unmeltable” , Popular Science (May , 2004) , p. 134 [JPEG image](#) (479 KB) .

[41](#) The theoretical consequences of discovering  $\text{Li}^{+[*]}\text{Si}_2\text{O}_4$  and/or  $\text{Cu}^{+[*]}\text{Si}_2\text{S}_4$  to be a high temperature superconductor would be profound . If singlet free , unassociated electrons were indeed their charge and energy carriers in the superconducting state , the implication would be that the venerable Cooper pairs should then be considered as a **subset** of the more general class of free , unassociated electrons in Drude electron materials .

[42](#) J.L. Bredas and G.B. Street , “Polarons , Bipolarons , and Solitons in Conducting Polymers” , Acc. Chem. Res. 18 (10) , pp. 309-315 (1985) [DOI](#) ; [PDF](#) (1798 KB) .

[43](#) Legal disclaimer , for which I apologize : The author of this document is not responsible for any injury or loss of any kind brought about using information presented in it . Furthermore , information presented in this document is intended for noncommercial educational purposes only , and the author will assume no liability (expressed or implied) whatsoever for any use or misuse of such information contained herein .

[44](#) W.A. Little , “Possibility of Synthesizing an Organic Superconductor” , Phys. Rev. 134 (6A) , pp. A1416-A1424 (1964) [DOI](#) ; idem. , “Superconductivity at Room Temperature” , Scientific American 212 (2) , pp. 21-27 (February 1965) [DOI](#) .

[45](#) W.A. Little , “The Exciton Mechanism in Superconductivity” , pp. 17-26 in W.A. Little (ed.) , Proceedings of the International Conference on Organic Superconductors , J. Polymer Sci. , Part C , Polymer Symposia 29 , Interscience , New York , 1970 [DOI](#) ; the quotation is from p. 26 .

The Figures are presented in the following nine pages .

Figure 1 :

\* return to the text on page [6](#) that first referred to this Figure .

### Physical Properties of Mixed-Valent Compounds

<u>Class</u>	<u>Optical</u>	<u>Electrical</u>	<u>Magnetic</u>	<u>Spectra</u>
I	colorless to medium colors	insulator	diamagnetic , paramagnetic	constituent atoms
II	deep blue , black	semiconductor poor conductor	ferro- , anti- ferromagnetic	constituent atoms
IIIA	intense colors	insulator	magnetically dilute	not of constituent atoms
IIIB	opaque , metallic luster , colours	metallic conductor	diamagnetic , ferromagnetic , Pauli paramagnetic	not of constituent atoms

Adapted from : M.B. Robin and P. Day , “Mixed Valence Chemistry – A Survey and Classification”, Adv. Inorg. Chem. Radiochem. **10** , pp. 247-422 , H.J. Emeléus and A.G. Sharpe (eds.) , Academic Press , New York , 1967 ; Table III , “Characteristics of the Four Classes of Mixed Valence Compounds”, p. 268 .

Figure 2 :

\* return to the text on page 9 that first referred to this Figure .

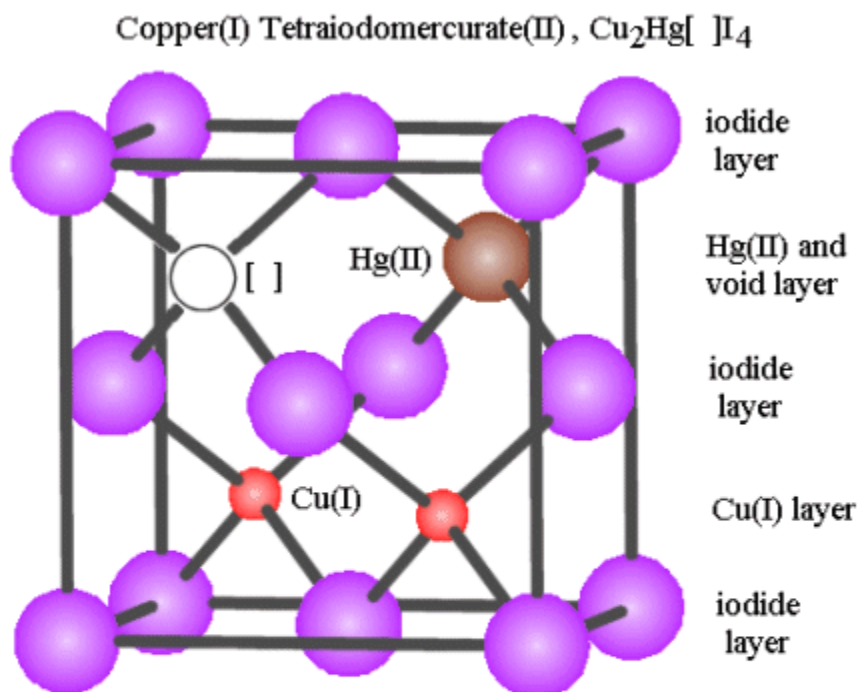
A Selection of Heavier Elements with  $ns^2$  Inert Pairs

<u>Element</u>	<u>Lower <math>ns^2</math> Valence</u>	<u>Higher <math>ns^0</math> Valence</u>	<u>Inert Pair</u>	<u><math>ns^0 E^0_{red}</math></u>
Mercury (*)	Hg(0)	Hg(II)	$6s^2$	+ 0.851
Gallium	Ga(I) (reducing)	Ga(III)	$4s^2$	-0.67 ( $1^+/3^+$ )
Indium	In(I) (reducing)	In(III)	$5s^2$	-0.443 ( $1^+/3^+$ )
Thallium	Tl(I)	Tl(III)	$6s^2$	+1.252 ( $1^+/3^+$ )
Tin	Sn(II)	Sn(IV)	$5s^2$	+0.151
Lead	Pb(II)	Pb(IV)	$6s^2$	+1.6913
Arsenic	As(III)	As(V)	$4s^2$	+0.560 ( $H^+$ )
Antimony	Sb(III)	Sb(V)	$5s^2$	+0.671 ( $H^+$ )
Bismuth	Bi(III)	Bi(V)	$6s^2$	+1.759

(\*) The occurrence of mercury's  $6s^2$  inert pair in elementary  $Hg^0$  atoms makes it a somewhat unreactive noble metal with weak interatomic Hg-Hg bonds. Mercury is thus a low-melting (- 39 C), low-boiling (357 C), liquid metal at room temperature.

Figure 3 :

\* return to the text on page [11](#) that first referred to this Figure .



Note : [ ] represents a tetrahedral void space in the lattice .

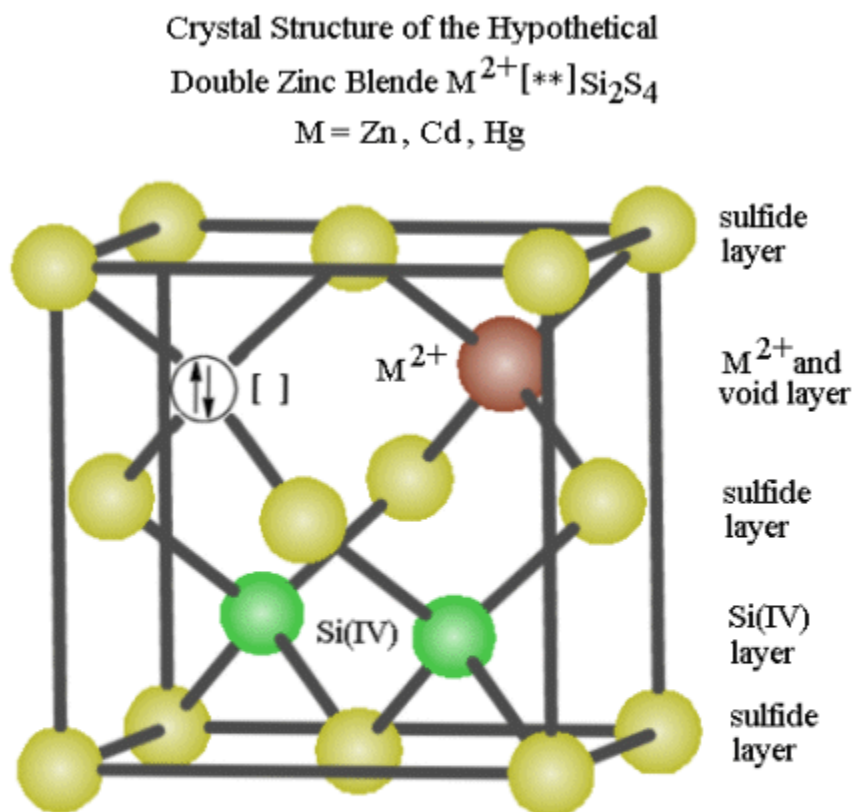
Ref. : "Thermochromism in the Ionic Conductor,  $\text{Cu}_2\text{HgI}_4$ ",  
p. 2 , Fig. 9.20C [this is the ordered , low temperature form] .

Download PDF (223 KB) from :


[http://people.umass.edu/~mjknapp/Chem242/  
2004%20Experiments/CuHg2I4Lab.pdf](http://people.umass.edu/~mjknapp/Chem242/2004%20Experiments/CuHg2I4Lab.pdf)

Figure 4 :

\* return to the text on page [12](#) that first referred to this Figure .



Note : [ ] represents a tetrahedral void space in the lattice.

 represents the  $ns^2$  valence electrons from the  $M^0$  guest atom, "popped" into the empty tetrahedral void space.

I have found it quite difficult with my basic molecular modeling software to draw **hexagonal** crystal structures, such as the wurtzites (cubic ones like zinc blendes are simple to make). An easy to visualize (ball-and-stick) molecular model of the wurtzite structure is presented in the ebook, "Crystallography Picture Book, Crystal Structures" [[PDF](#), 2808 KB], by Dr. [Steffen Weber](#) (unpaginated, but the model is on PDF p. 18).

Figure 5 :

\* return to the text on page [12](#) that first referred to this Figure .

**A Cooper Pair of Electrons is Suspended  
in the Center of a Tetrahedral Void Space  
in a Wurtzite by Four Sulfide Electron Pairs**

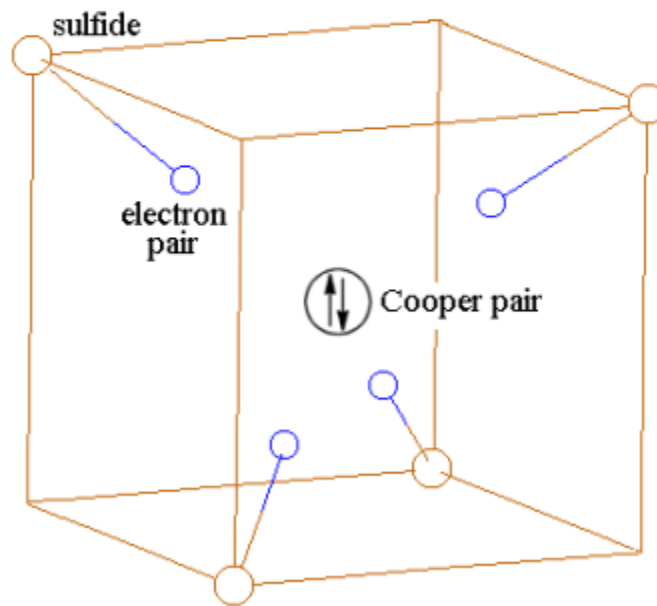


Figure 6 :

\* return to the text on page [14](#) that first referred to this Figure .

### Location of Mercury's $6s^2$ Electrons in $\text{Hg}^{2+}[\text{**}]\text{Si}_2\text{S}_4$

– **three** possible locations –

**xx** = mercury's inert pair ( $6s^2$ ) of electrons ;

**oo** = sulfur electron pairs in  $\text{S} \rightarrow \text{Hg}$  bonds .

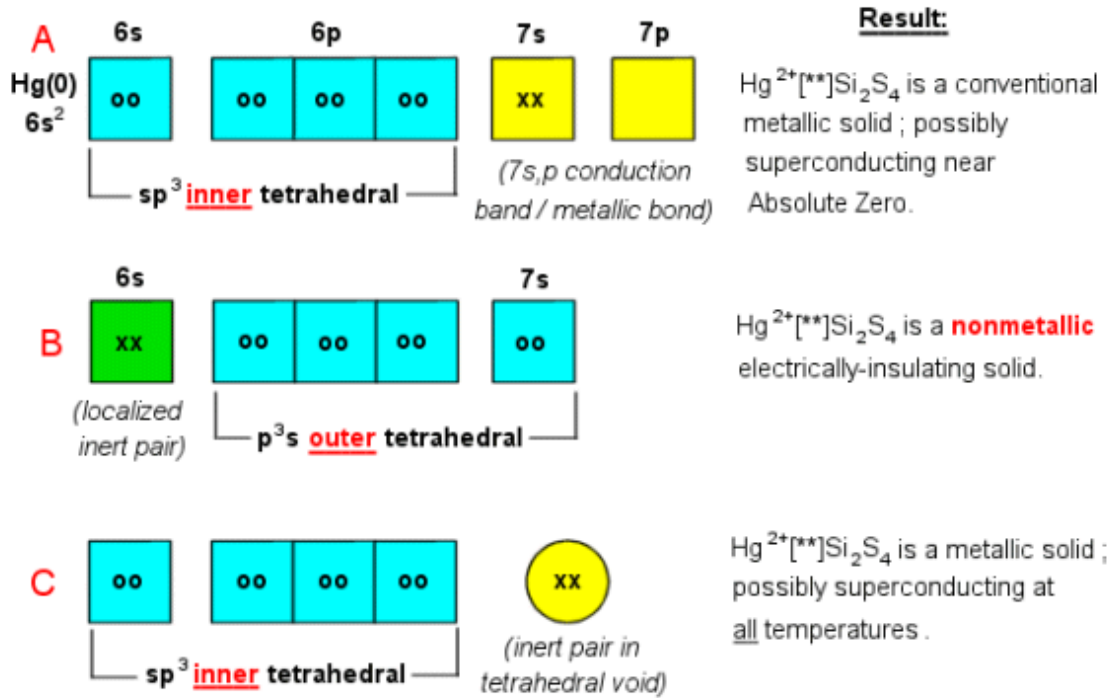




Figure 7 :

\* return to the text on page [20](#) that first referred to this Figure .

White Silica Sand and Zinc Ingots



Left photo : piles of pure , white silica sand , copied from the Wikipedia web page "Silicon dioxide", at [https://en.wikipedia.org/wiki/Silicon\\_dioxide](https://en.wikipedia.org/wiki/Silicon_dioxide) . Right photo : stacks of zinc ingots in a warehouse , from the web page "Daxin Metal Maiteng Co. Ltd.", at [http://hebeifuhua0311.en.ec21.com/offer\\_detail/Sell\\_zinc\\_ingot--20258582.html](http://hebeifuhua0311.en.ec21.com/offer_detail/Sell_zinc_ingot--20258582.html)

My thanks to the authors and/or copyright holders of these pictures .

Figure 8 :

\* return to the text on page [22](#) that first referred to this Figure .

**Betaine–Electride Design Concept**

(illustrated for trimethylglycine betaine and sodium electride)

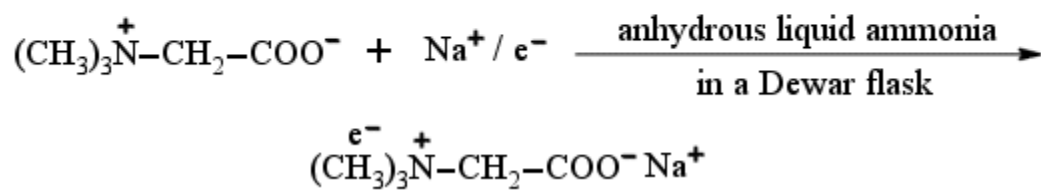
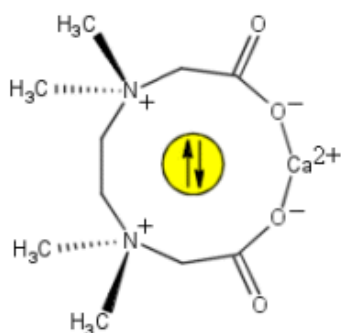


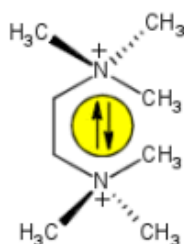
Figure 9 :

\* return to the text on page [22](#) that first referred to this Figure .

**Several Proposed Organic Electrides**  
 — containing pairs of free , unassociated electrons —



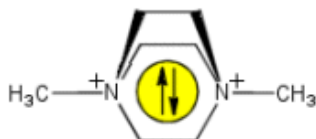
calcium TMEDA-bis-  
carboxylate-2e-electride



1,2-bis(trimethylammonium)-  
ethane-2e-electride



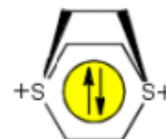
N,N,N',N'-tetramethyl-  
piperazinium-2e-electride



N,N'-dimethyldabconium-  
2e-electride



disodium dabconium-  
N,N'-bis-oxide-2e-electride



triethylene bis-sulfonium-  
2e-electride

Note : TMEDA is N,N,N',N'-tetramethylethylene diamine (b.p. 120-122 °C), a common and modestly priced organic reagent ; "dabconium" is the quaternized form of DABCO, 1,4-diazabicyclo[2.2.2]octane, or triethylene diamine (m.p. 158 °C), a modestly priced industrial organic chemical , used as a strongly basic catalyst in the manufacture of polyurethane foams , paints , and varnishes .