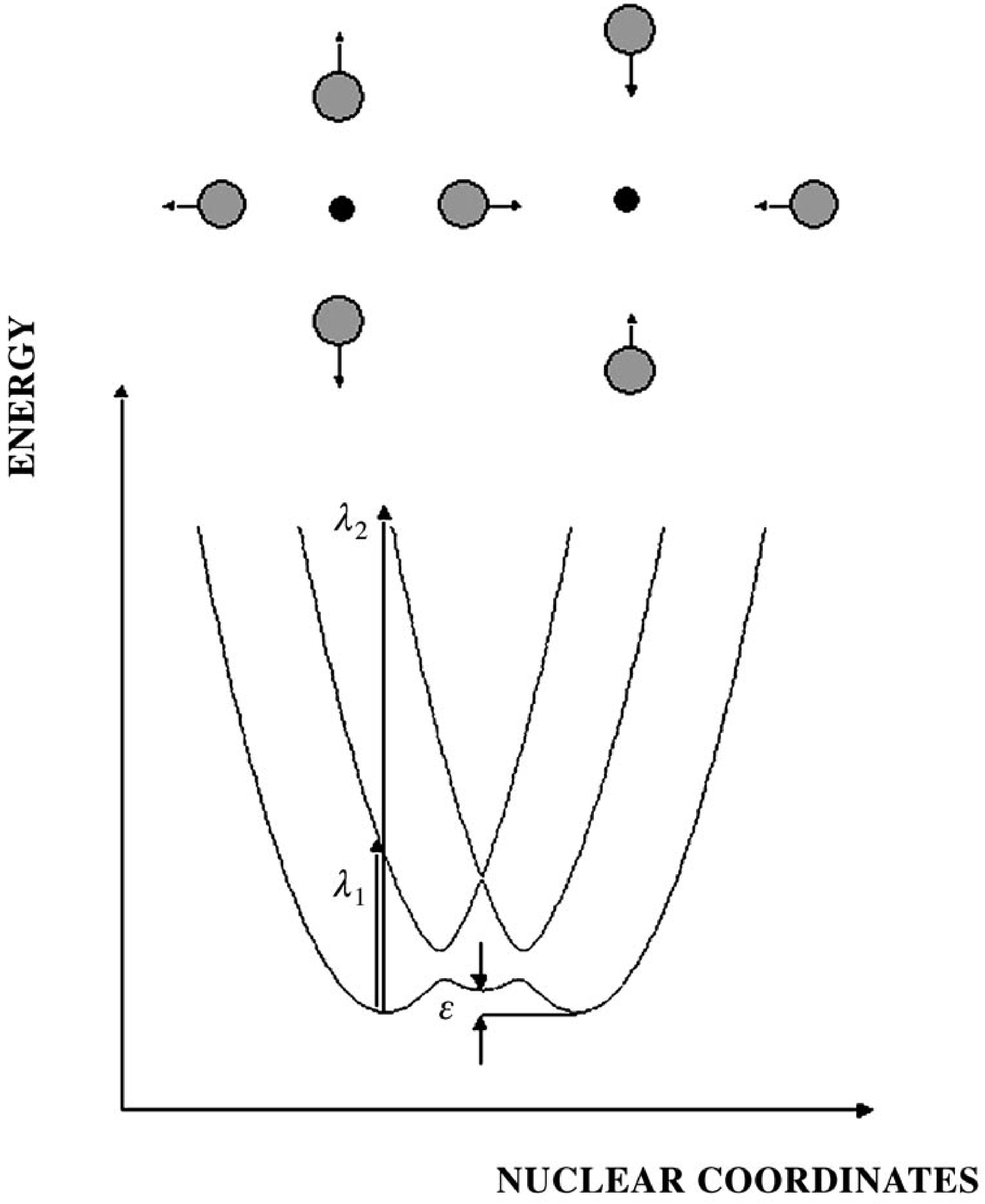
SUPERCONDUCTIVITY IN COINAGE METAL COMPOUNDS



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Superconductivity in Copper, Silver, and Gold Compounds

Sven Larsson*[a]

Abstract: High-temperature superconductivity exists in layered, square-planar cuprates, but is almost absent in most other Cu^{II} compounds and in most Ag^{II} and Au^{II} compounds. Valence state II is quite unusual in silver and gold and often disproportionates to valence states I and III ("negative-U compounds"). The two-electron difference in oxidation state is suggestive of electron pairing, a prerequisite for superconductivity. In the present paper the connection between disproportionation and geometrical structure on one hand and superconductivity on the other is discussed by using the accepted theory for mixed valence complexes. It is concluded that absence of superconductivity in gold and silver compounds can be connected to the instability of oxidation state II and the large difference in equilibrium geometry between oxidation states I and III.

Keywords: copper • gold • mixed-valent compounds • silver • superconductors

Introduction

High-temperature superconductivity was discovered in $La_{2-x}Ba_xCuO_4$[1] and somewhat later, with a very high critical temperature, in $YBa_2Cu_3O_{7-x}$.[2] Since equally charged atoms in the same group of the periodic table tend to have similar chemical and physical properties, d^9 systems corresponding to Ag^{II} and Au^{II} might be expected to form superconducting compounds in the same way as Cu^{II}, as discussed by Sleight,[3] and Grochala and Hoffmann.[4] In reality Ag^{II} and Au^{II} systems usually do not support superconductivity. This might be due to differences in size and ensuing structural differences. In silver compounds superconductivity has been found only in Ag_7O_8X, in which $X^- = NO_3^-$, F^- or BF_4^-, with a low critical temperature.[5] Superconductivity exists also in disulphides, diselenides and ditellurides[6,7] of copper, silver and gold. Since superconductivity occurs also in the elements S, Se and Te, the important atom may be the chalcogenide atom in this case rather than the coinage metal atom. Compounds of S, Se, and Te therefore left out of the discussion here.

In Ag^{II} compounds with fluorine ligands, such as $CsAgF_3$ and Cs_2AgF_4, planar sheets are formed within the crystal as in the superconducting cuprates,[8] but superconductivity has not been reported. This is also the case for tertiary Cu^{II} fluorides[9,10] and CuF_2.[11] An evident difference is that the mentioned fluorides are stoichiometric (d^9), while the formal number of d electrons in the superconducting cuprate planes usually is less than nine per metal atom, depending on doping. If $x = 0.5$ in $YBa_2Cu_3O_{7-x}$ all copper atoms in the plane are in oxidation state II, but the compound is not a superconductor. Thus the density of states at the Fermi level is of evident importance for superconductivity, but it is not known exactly how. It could be directly, by occupancy of orbitals, or indirectly, if the geometric structure depends on the number of electrons. It is well known that a rather small change in the orbital occupancy of the localized, antiferromagnetic state may lead to a delocalised, superconducting state.

In the layered compounds $CsAuX_3$ or Cs_2AuX_4 (X = Cl, Br, I), the geometry suggests Au^I–Au^{III} mixed valence.[12] The electron count corresponds to exactly one hole per site. $CsAuX_3$ and Cs_2AuX_4 are semiconductors (at low pressure) with large activation energies.[13,14] The conductivity is nonmetallic, but increased by several orders of magnitude at high pressures of a few GPa;[13–16] however, superconductivity has not been reported.

Silver is more stable in valence state II with fluorine rather than oxygen as ligands, and F^- is close to O^{2-} in its ligand field effects. Grochala and Hoffmann in an interesting paper[4] have pointed out a number of silver fluoride structures, which they hypothesise might possess superconducting properties in doped form or with a different second metal ion (in tertiary compounds). Their conditions for possible superconductivity are rather mild and based on mixed valence (MV) between two successive oxidation states, in this case Ag^I/Ag^{II} or Ag^{III}/Ag^{II}. The conditions of the present paper are more restrictive.

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[a] Prof. S. Larsson
Department of Chemistry
Chalmers University of Technology
412 96 Göteborg (Sweden)

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Connections between mixed valence and superconductivity have been suspected for a long time, even before the advent of the high T_c cuprates (T_c = critical temperature) in 1986.[17,18] At first the cuprates were not connected to mixed valence, since valencies I and III cannot be identified in the superconducting state. Nevertheless Wilson considered the existence of three oxidation states for copper in general as relevant for the occurrence of superconductivity in doped La_2CuO_4 and $YBa_2Cu_3O_7$.[19] Simon,[20] Sleight,[3,21] Bussman–Holder et al.,[22] Burdett[23] and Brandow[24] put forward similar ideas. The present author connected activation barrier and resistivity to geometry changes in three oxidation states.[25,26] Prassides,[27] de Jongh[28] and others[3,24–31] have discussed doped $BaBiO_3$, in which oxidation states III and V are involved on the bismuth atom, using similar arguments. The mentioned "valence-fluctuation models"[19–31] are different in details, however.

Band models cannot be easily applied to mixed valence systems. In a d^8–d^{10} system, the Fermi level should be in the d^8 band in spite of the expected higher ionisation energy for a more highly charged ion Au^{III}. Furthermore d^8 systems like NiO are often insulators in spite of the fact that the Fermi level is located in a continuous d-band. Mott has suggested a solution to this problem by comparing coupling to interelectronic repulsion (U),[32] measured as the difference between electron affinity and ionisation energy. The latter quantity is zero for a metal and a few eV for an insulator. In any case experimentally measured characteristics can hardly be used to predict the same property. For this reason the Mott model will not be used in the present paper.

Localization is rather easy to predict theoretically in a finite mixed-valence system. If it cannot be directly calculated one may compare coupling ($t = \Delta/2$) and reorganization energy (λ) in the Marcus–Hush model[33–35] (Figure 1). On the experimental side Creutz has convincingly shown that the Creutz–Taube complex is delocalized, while similar $Ru^{II/III}$ complexes with longer bridges are localized.[36] This result is consistent with the Marcus–Hush model, for which a large ratio Δ/λ leads to disappearence of the activation barrier and delocalization. Larsson and Klimkāns suggested an extended model for the infinite case.[37] This model may also be used for two-electron transfer in superconductors, although this problem is more complicated.

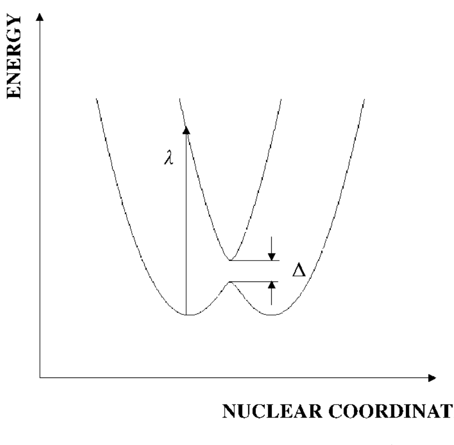

Figure 1. Potential-energy curves in the MV-2 case. λ is the reorganization energy. The left-hand parabola corresponds to the oxidation states v and $v+1$ on the two sites and the right-hand parabola to oxidation states $v+1$ and v.

Theories on systems in which three consecutive oxidation states are involved in ground states or in low excited states will here be called MV-3 theories, as opposed to MV-2 theories, in which only two oxidation states are involved. The lowest and highest oxidation states, different in two electrons, are of relevance to electron-pair transfer (EPT) [Eq.(1)]:

$$^{*}M^{(n+1)+} + M^{(n-1)+} \rightarrow {}^{*}M^{(n-1)+} + M^{(n+1)+} \tag{1}$$

It is easy to think of a mixed valence system in which half the sites have the lower oxidation state and the alternating, equivalent sites have the higher oxidation state. We may view the electron pair transferred in Equation (1) as the localized version of the Cooper pair. We thus use as a working hypothesis that "chemical pairs" in a repetitive structure act as Cooper pairs if they are delocalized in the sense of Hush.[34,35] The pairing discussion is carried out in the localized, simplified form. Delocalization of the pairs is treated as a separate problem.

It turns out that delocalization of a chemical pair strongly depends on the intermediate oxidation state.[25] Chemically the intermediate oxidation state belongs to the "comproportionated" left-hand member in Equation (2).

$$2\,M^{n+} \leftrightarrow M^{(n+1)+} + M^{(n-1)+} \tag{2}$$

The disproportionated phase of the right-hand member corresponds to the "negative-U" state, a term used in solid-state physics. That the Mott parameter U in some cases may be negative illustrates the difficulties with too simplified models. Alternative terms are "charge density wave" (CDW) or a "charge-ordered" phase. Both have appeared in connection with superconductivity. In the present model the CDW state is the localized version of the superconducting state. The comproportionated phase may be antiferromagnetic and form a spin density wave (SDW). According to the present model superconductivity arises if the CDW and SDW states have about the same energy and similar equilibrium geometries.[25,26]

A microscopic description of a finite CDW–SDW system may be achieved by using quantum chemical methods that include correlation effects in a many configuration treatment, for example, CASSCF.[38] In the square-planar case a "gedanken" calculation of finite square systems with $(2L)^2$ (L is a natural number) equivalent sites and $(2L)^2$ active electrons would result in electronic states in the form of potential-energy surfaces (PESs). Geometry optimisation under the restriction of square planarity and equal distances between the sites, but with no restrictions on metal–ligand distance on the different sites, would lead either to SDW, CDW, or a common vibronic ground state. In the last case and the SDW case the metal–ligand distances would be the same and in the CDW case alternating. The coinage metal group provides a number of examples of these two cases, since oxidation state II is gradually less stable in the series copper→silver→gold. The third phase with a common vibrational ground state appears as a clear possibility. This phase, if delocalized, would have the properties of a superconducting phase.[25]

Theoretical Models for Two-Site MV-2 and MV-3 Systems

MV-2 theory is based on the well-known electron-transfer (ET) models of Marcus (Figure 1),[33] Holstein[39] and Piepho et al.,[40] while the MV-3 model is an extension based on a model of Prassides and Day.[41] Electron-pair transfer (EPT) between two equivalent sites may be described by PESs, corresponding to the site occupations ($v-1,v+1$) and ($v+1,v-1$), with equivalent minima (Figure 2). Each minimum corresponds to localization of the electron pair to either of the two metal sites. Vertical excitation (λ_1) from the lower to the upper energy surface is equivalent to ET between the two metal atoms, leading to equivalent sites.

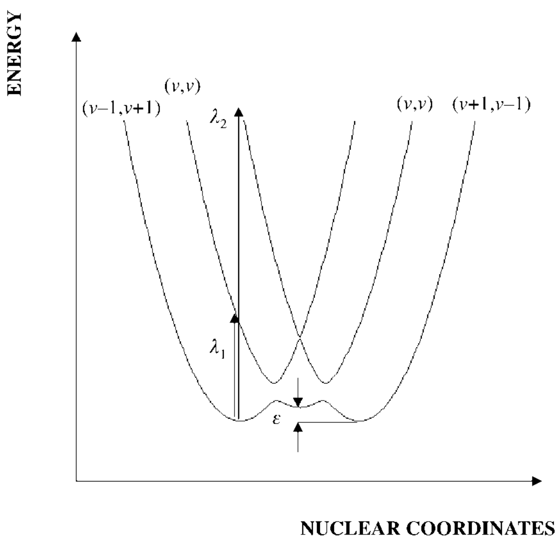

Figure 2. Potential-energy curves in the MV-3 case. λ_1 and λ_2 are reorganization energies for the transfer of one or two electrons, respectively. v is the valence state of the comproportionated state and $v-1$ and $v+1$ of the disproportionated state. The latter state is here assumed to be lower in energy in the figure (negative-U state). For Cu^{II} systems the (v,v) curve is probably lower (and for Au^{II} systems higher) relative to ($v+1,v-1$) and ($v-1,v+1$) than shown in the figure.

The classification scheme of Robin and Day[42] for MV-2 systems can be rather well extended to MV-3 systems, as follows:

1) In Class I the sites are nonequivalent and cannot be interchanged by changing bond lengths, in other words cannot comproportionate.
2) In Class II there is an activation barrier for EPT due to geometry difference between the oxidation states, implying localization and electrical resistance. Applied pressure leads to smaller differences and a lower barrier. The absorption spectrum is partly due to site interactions.[43]
3) Finally in Class III systems the charge is delocalized. If the SDW and CDW energies are similar at $T=0$, the vibronic interactions lead to superconductivity, according to the hypothesis. If the energies agree at an elevated temperature, delocalization only appears in a narrow temperature window at the phase transition.

The reorganisation energy λ (eV) is defined as the sum of energy relaxations after one (or two) electron has been added at the site of the higher oxidation state and removed from the other. λ may be written as Equation (3).

$$\lambda = \sum_i {}^1\!/_2 k_i \delta d_i^2 \approx 15 \sum_i \delta d_i^2 \tag{3}$$

The summation extends over all bond length (and possibly bond angle) changes (δd_i) on both sites. In the approximate expression of the right member, δd_i should be given in Å. The force constant used corresponds to a vibrational wave number of 500 cm^{-1} and an effective mass of 16 atomic units.

When interactions are "switched on", the PES intersections become avoided crossings. The effective coupling is half of the gap ($H_{12}=\Delta/2$) between the interacting PESs. The usually large ET coupling in MV-2 systems leads to a decreased activation barrier (E_a). In the symmetric case E_a decreases from $\lambda/4$ at $|\Delta|=0$ to zero at $|\Delta|=\lambda$ [Eq. (4) if $|\Delta|<\lambda$].

$$E_a = \frac{(\lambda-|\Delta|)^2}{4\lambda} \tag{4}$$

Similarly large coupling at asymmetric CDW–SDW crossings may lead to a disappearing activation barrier. The coupling corresponding to EPT is very small unless the PES corresponding to equal oxidation states, the (v,v) state in Figure 2, is involved at about the same energy as the CDW state.[25,29]

Oxidation states are defined by the geometry and charge of the site. The most important single factor connected to the oxidation state of a metal ion site is the average metal–ligand distance. At the respective energy minima, the sites have distances typical for the different oxidation states (if $|\Delta|$ is small). The average metal–ligand distance is smaller the larger the oxidation state. The "reaction path" for ET or EPT therefore involves metal–ligand distance increase at one site and decrease at the other. In the right-hand minimum of Figures 1 and 2, the equilibrium geometries and oxidation states are swapped. The most important vibrational modes of this reaction coordinate are the breathing modes $\approx$500 cm^{-1}. These modes give the coupling between electrons and nuclei in their motion because of the direct connection to the oxidation states. Bussman-Holder et al. have considered other possibilities for geometrical fluctuation.[30]

The oscillator strength of the vertical intervalence transition ($v+1,v-1$)→($v-1,v+1$) is very small, since the wave functions are different in two spin orbitals. However, if the PESs of the SDW and CDW intersect, large oscillator strengths are obtained for transitions between CDW and

SDW. Strong absorption in MV-3 complexes consequently strongly suggests that the (v,v) state (SDW) is present.

A well-known MV-3 system is Setterberg's complex Cs_2SbCl_6. The two different Sb sites correspond to the valence states Sb^{III} and Sb^{V}.[41] Since Cs_2SbCl_6 is strongly blue, Sb^{IV} is involved as an excited state. Prassides and Day have simulated an intervalence spectrum with great success[41] by assuming that it arises from a transition of the type $Sb^{III}+Sb^{V}\rightarrow 2\,Sb^{IV}$ and energy λ_1 (Figure 2). Since $Sb^{III}+Sb^{V}$ is the ground state, Cs_2SbCl_6 is a "negative-U" compound. The bond lengths are very different[38]: $Sb^{III}{-}Cl = 2.646$ Å and $Sb^{V}{-}Cl = 2.384$ Å. The difference (0.26 Å) leads to $\lambda = 12$ eV by Equation (3), since twelve bonds are changed.

Other examples of MV-3 systems are $Ba_{1-x}K_xBiO_3$ and $BaPb_xBi_{1-x}O_3$.[44–45] As the doping levels are increased (increased value of x) the system changes from a typical class II to a class III system, that is, from localized CDW to a delocalized superconductor.[46] The main reason is probably that increased doping leads to equalization of metal–ligand bond lengths and, hence, lower reorganization energy. If, for example, $\delta d = 0.02$ Å is used in Equation (3) for 12 bonds, we obtain $\lambda = 0.07$ eV, which is of the same order of magnitude as the vibrational energy. The coupling remains the same and therefore the ratio Δ/λ increases; this is favourable for an insulator-to-metal transition.[37] For $x = 0$ ($BaBiO_3$) the two sites correspond to Bi^{3+} and Bi^{5+} sites as in the case of Cs_2SbCl_6.[44–46]

As mentioned above disproportionation is common in the case of silver and, particularly, gold. Ag^{II} systems are not disproportionated in fluorides at low temperatures.[4,8,11,47,48] Wells' salt, $CsAuCl_3$, is probably the first and best-known example of disproportionation in gold compounds.[12–16] At normal pressure the distances of the xy plane are 0.4 Å smaller in $Au^{III}{-}Cl$ than corresponding distances in $Au^{I}{-}Cl$. Along the z axis only Au^{I} forms a bond to Cl^-. The distances are 2.31 Å for $Au^{I}Cl$ and 3.13 Å for $Au^{III}Cl$.[12] In $CsAuCl_3$ the activation barrier for direct EPT is, hence, very large.

Importance of the Jahn–Teller effect

The phonon coupling typical for superconductivity is sometimes mixed up with the Jahn–Teller (JT) effect. The JT theorem states that degeneracy of the ground state is removed by nuclear distortions, leading to a ground state with lowered symmetry and energy. This is of importance for superconductivity in the layered perovskite case, since the shorter bonds between copper and oxygen (≈ 1.9 Å) are always in the same CuO_2 plane, while the longer bonds (≈ 2.1 Å) are perpendicular to this plane. This way the most antibonding, singly unoccupied spin orbital is always in the plane and this restricts conductivity to this plane. If the JT distortion is in different directions superconductivity is hindered.

The "second-order JT effect" (SOJT) refers to a nondegenerate case with mixing of the ground state and a low-energy excited state. The JT and SOJT theorems do not suggest anything about the extent of the distortions, only that distortions may take place. The difference between two JT geometries may be so small that there are common vibrational levels. In this sense the JT and SDW–CDW distortions behave similarly. However, JT and SOJT distortions refer to a single site, while the SDW–CDW distortions extend over at least two sites.

Delocalization

Transition metal oxides are usually localized and spin ordered. Cu^{II} and Ag^{II} oxides are d^9 systems, and as such very often SDW systems with one hole per site. If the hole has spin up on one site, the alternating site has spin down. The orbital product may symbolically be written as $(\uparrow o \times o \downarrow)$, where o denotes an empty spin orbital.

After symmetrisation the two-site disproportionation may be written as Equation (5):

$$(\uparrow o \times o \downarrow) \pm (\downarrow o \times o \uparrow) \leftrightarrow (oo + \uparrow\downarrow) \pm (\uparrow\downarrow + oo) \qquad (5)$$

In the CDW state on the right, the electrons are paired on a single site. If "a" is the orbital on left and "b" the equivalent orbital on the right, α = spin up and β = spin down, we may write Equation (6):

$$(ab + ba)(\alpha\beta - \beta\alpha)]/2 \rightarrow (aa \pm bb)\ (\alpha\beta - \beta\alpha)/2 \qquad (6)$$

On the left-hand side the oxidation states are the same for the two sites and therefore the metal–ligand bond lengths are also the same. In the localized CDW-phase unsymmetric functions are obtained on the right-hand side, either $aa(\alpha\beta-\beta\alpha)$ or $bb(\alpha\beta-\beta\alpha)$.

Since we normally find a metallic phase between the insulator and superconductor phases, the fact that the localized SDW and CDW phases occur close to the delocalized, superconducting phase in cuprates was a surprising discovery. Furthermore the Mott–Hubbard U is supposed to be small or even negative for high T_c superconductors, but CuO is not a metal and hence $U \gg 0$. The solution of Edwards et al. to this problem is that the insulator–metal and insulator–superconductor delocalization occur under the same conditions.[49] In the present paper a more radical view is taken, whereby the Mott model for localization is abandoned and replaced by a more realistic model that includes nuclear coordinates.[31] Since MV-3 theory requires interaction between SDW and CDW for both superconductivity and delocalization, there is no reason to assume a metallic phase between the insulating and superconducting phase. Ordinary metals correspond to the delocalized MV-2 case.

Delocalization of charges need not occur under the same conditions as delocalization in absorption spectra. CuO is black, but not NiO. Both are insulators. In the Bloch model both CuO and NiO are delocalized. The Bloch model is simply nonapplicable for these "strongly correlated" systems. In NiO the local triplet wave function has a lower energy than the delocalized metallic one. The triplets interact to form the antiferromagnetic lattice, but this interaction does not lead to any broadening of the spectrum, since the bandwidth due to triplet–triplet interaction is too small. In the d^9 systems this is completely different, since the site interactions are of one-electron type and large. Finally the d–d transitions in Au^{III} d^8 systems are of a singlet type, but at too high an energy to cause absorption in a large part of the visible spectrum. In a mixed valence Au^{I}–Au^{III} system the black absorption is instead due to intermetal mixed-valence transitions.[34,43]

Application to Superconductivity in Coinage Metal Systems

We will now go through some relevant copper, silver and gold oxides and their salts to try to correlate conductivity properties with site, crystal and electronic structure on the basis of MV-3 theory, extended as described above and in earlier papers.

Cuprates: The superconducting Cu^{II} systems La_2CuO_4 and $YBa_2Cu_3O_7$ have square-planar layers with copper octahedrally coordinated to oxygen. The axial bonds to the oxygen atoms in the neighbouring layers are always the long bonds.[50] Therefore, the half-empty orbital is always the $3d_{x^2-y^2}$ orbital, along the bonds of the CuO_2 x,y plane. This ordering is important for superconductivity, since σ-currents are then possible in a perpendicular magnetic field.[25]

The corresponding Ag^{II} systems have not been made. This may depend on the fact that the Ag^{II} ion is larger than the Cu^{II} ion and, therefore, does not fit with the intervening layers. If square-planar Ag^{II} layered systems can be made, they are not necessarily superconducting, since the valencies may still be localized.

CuO: CuO has a tenorite structure in which each Cu^{II} is surrounded by four coplanar bonds.[51,52] However, no layered plane structure is formed as is the case in La_2CuO_4 and $YBa_2Cu_3O_7$. The half empty $3d_{x^2-y^2}$ orbital is in the local plane, but corresponding orbitals on different sites are not in the same plane. CuO is antiferromagnetic (SDW) in the ground state. The tenorite structure appears to be an important reason why CuO is not superconducting.

AgO: AgO is not much different from CuO in structure, except that there are two different sites. In one of the sites there are two neighbouring oxygen atoms at 2.18 Å and two very distant oxygen atoms at 2.66 Å. This is evidently an Ag^{I} site. The other site has four coplanar oxygen neighbours at 2.05 Å, evidently an Ag^{III} site.[53] The system is diamagnetic, which confirms that Ag^{II} in AgO is disproportionated into Ag^{I} and Ag^{III}. AgO thus has a CDW ground state, apparently with a high activation barrier for EPT.

AuO: AuO is not known. The only stable gold oxide seems to be Au_2O_3 with valency Au^{III}.

Ag_7O_8X: This chemical formula represents a number of cage structures[54] that are metallic and superconducting below 0.1–2 K (if $X^- = NO_3^-$, F^- or BF^-).[5,54] In this case there are several phase transitions at lower temperatures. At least for $X^- = NO_3^-$ there is a cubic to tetrahedral rearrangement at about 180 K and this compound also has the highest T_c. The cubic structure determined at room temperature[54] cannot be expected to be superconducting, since the sites are nonequivalent.

CuF_2: CuF_2 forms a distorted rutile structure.[11] The Cu site is typically Jahn–Teller distorted and has four coplanar bonds of length 1.93 Å and two axial ones of length 2.27 Å. There is no common square plane and the ground state is SDW.

AgF_2: α-AgF_2 is stable at low temperature and has a typical Jahn–Teller distorted Ag^{II} site with four short bonds (2.07 Å) and two long bonds (2.58 Å). The structure is a puckered sheet. The spin structure is complicated.[4] β-AgF_2 is stable at a high temperature and has mixed valence with a CDW ground state.[47] The two phases are thus very different, but there is a phase transition at elevated temperatures. At a low temperature the energies of the SDW and CDW phases are apparently very different, so superconductivity is not expected.

Ternary copper fluorides: $KCuF_3$ and K_2CuF_4 are typical Cu^{II} systems, with elongated or compressed Jahn–Teller distortions. These compounds are not diamagnetic, but have a complicated magnetic structure. The Jahn–Teller effect is large.[9,10] In fact there are normally three different metal–ligand bond lengths in the octahedron around the metal ion. The disproportionated CDW state is not available at low energy, as is clear from the weak colour, hinting to the absence of charge transfer and intermetal spectra.

Ternary silver fluorides: $AAgF_3$ and A_2AgF_4 (A = K, Rb, Cs) are typical Ag^{II} systems, shown by the absence of diamagnetism. The colour is strongly blue–brown metallic, indicating a delocalized system. Jahn–Teller distortions are ordered:[4,8] Ag–F 2.06–2.13 Å or 2.42–2.51 Å. Why is it not superconducting? Apparently the comproportionated phase is lower in energy than its disproportionated counterpart,[47] but the strong absorption suggests that the silver system is not as high in energy as in the corresponding copper case. The Ag^{III} site would be square-planar, whereas the Ag^{I} site would be octahedral or linear. Probably the geometry differences between the disproportionated and comproportionated phases are too large to allow common vibrational levels, and thus there is no superconductivity.

It might be added that if the sites are compressed instead of elongated along the z axis, the coupling between the sites is decreased, but this should not by itself prevent superconductivity.

Ternary gold halides—$AAuX_3$ and A_2AuX_4: Superconductivity may be expected in $AAuX_3$ or A_2AuX_4 compounds, which are iso-structural with $BaBiO_3$.[16,55] In this case the conductivity has been found to increase very much under pressure. This is easy to understand by using the model described here, since the metal–ligand bond length for different oxidation states becomes less different under pressure.

In fact the results by Kojima et al.[16,43,55] prove that this model is correct. An important difference to the $BaBiO_3$ systems is that there does not seem to be any doped Au compounds. Doping might be possible with Pt^{2+} ions, which are also d^8 systems with low spin, but this has probably never been tried. The absence of superconductivity in the temperature ranges studied may also be caused by the high energy of the Au^{II} state, independent of pressure.

The comparison between the ternary compounds of silver and gold is interesting, since the former are more stable in oxidation state II and are, therefore, magnetic, while the gold compounds are more stable with mixed I and III valence. The structures are ideal for superconductivity, but either the energy or the geometry differences (or both) to the other phase (I and III for silver and II for gold) are too large.

In summary the copper fluorides do not disproportionate. The same is the case for CuO. AgF_2 and the silver oxides do disproportionate and there is one example of a superconductor at a low T_c. Possibly the propensity of copper to disproportionate in an oxygen-rich environment is also high, although no CDW state has been found as ground state. This conclusion is consistent with the fact that binary or ternary copper systems can be made with copper in all three oxidation states with oxygen ligands. It is thus not too far-fetched to suggest that the superconducting cuprates are indeed delocalised MV-3 systems.

Conclusion

A great number of oxide and related superconductors are related to compounds in which the metal ion valencies are distinct and mixed.[3,4,17–31] Here it is shown how three oxidation states in a row may promote superconductivity. All three oxidation states must appear in low spin. $Ni^{2+}/Ni^{3+}/Ni^{4+}$ does not qualify, since Ni^{2+} prefers a high spin (triplet) ground state. In the case of $Cu^{+}/Cu^{2+}/Cu^{3+}$ Cu^{+} and Cu^{3+} have low spin, while the Cu^{2+} sites in CuO and other oxides have alternant spin (antiferromagnetic compound if not superconducting). These copper systems therefore satisfy the spin condition. This is also the case for ${C_{60}}^{2-}/{C_{60}}^{3-}/{C_{60}}^{4-}$ in A_3C_{60}.[29]

Several silver and gold compounds, for example several Au^{I}–Au^{III} mixed valence compounds, also satisfy the spin condition, but are not superconductors. At the same time typical superconductors do not appear to be mixed valence systems (the cuprates). This can be understood if it is realized that disproportionation, common in gold compounds, usually leads to equilibrium structures that are very different between the oxidation states at the metal sites. Furthermore no suitable dopant has been found so far for these compounds. On the other hand, when superconductivity exists, delocalisation makes the direct connection to mixed valence less evident.

Superconductivity as well as delocalization is connected to electron nuclear coupling as in the well-known Marcus–Hush model.[33–35] Electron pairs move without activation energy and resistance if SDW and CDW are involved at about the same energy and interact through the vibrational motions. The final ground state vibronic wave function is delocalized and has an energy gap to the first excited state. Grochala et al.[56] and Klimkāns and the present author[57] have calculated the vibronic states relevant for internal ET, but not so far for EPT.

In the case of local EPT, the metal site changes its valency by two units. In order to have a large pair mobility and strong absorption of light, the intermediate valence state, corresponding to the SDW phase, has to be present at a low energy. Although this particular role of the SDW state is unique to the model used here, similar theories have recently been advanced to explain supercurrents of Cooper pairs in Josephson junctions.[58]

Correlation is generally considered as important for superconductivity. In the model advanced here, there are evident correlation effects, such as spin correlation in the SDW state and on-site correlation in the CDW state. The SDW–CDW interaction is also a typical correlation effect. Strong correlation effects are one reason why band models do not provide a good starting point for a discussion of superconductivity.

There are many structural reasons why silver and gold are less commonly involved in superconductivity than copper compounds. Furthermore, the heavier atoms tend to be less stable in oxidation state II than corresponding copper compounds. This leads to a favouring of the CDW state that appears to be the major reason for absence of superconductivity.

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