Influence of Valence, Electronegativity, Atomic Radii, and Crest-Trough Interaction with Phonons on the High-Temperature Copper Oxide Superconductors

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Several structural features, including electron transfer between atoms of different electronegativity, oxygen deficiency, and unsynchronized resonance of valence bonds, as well as tight binding of atoms and the presence of both hypoelectronic and hyperelectronic elements, cooperate to confer metallic properties and high-temperature superconductivity on compounds such as $(\mathrm{Sr,Ba,Y,La})_2\mathrm{CuO}_{4-y}$.

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The theory of superconductivity based on the interaction of electrons and phonons was developed about thirty years ago.[1-4] In this theory the electron-phonon interaction causes a clustering of electrons in momentum space such that the electrons move in phase with a phonon when the energy of this interaction is greater than the phonon energy $\hbar\omega$. The theory is satisfactory in most respects.

In the resonating-valence-bond theory of metals the electronic structure of the metal is described in successive steps involving integrals of decreasing magnitude.[5-9] First, two electrons with opposed spins and occupying orbitals on adjacent atoms form a covalent bond, which may have some ionic character. Second, these covalent bonds resonate among the alternative positions in the metal. Third, because of the principle of approximate electroneutrality,[10] an atom can assume only resultant charges +1, 0, or −1, corresponding to M^+, M^0, and M^-. (This restriction explains why Fröhlich[2] decided that all metals are effectively univalent.) The wave function for such a structure, describing the resonance of bonding electron pairs among alternative interatomic positions, was formulated in 1949.[6]

The resonating-valence-bond theory is in many ways equivalent to the conventional band theory of metals, but it has the advantage that it permits far more easily the discussion of the dependence of the properties of a metal on the nature of the atoms of which it is composed. For example, in 1968 I pointed out that there are two classes of superconductors, crest superconductors and trough superconductors.[11] We may consider the hypoelectronic metal La as an example. It has valence $v=3$, ligancy $L=12$, and superconductivity temperature 6 K. Its metallic radius[12] for $L=12$ is 1.865 Å, which decreases to 1.650 Å for La$^-$, which has valence 4; accordingly La is a crest superconductor, with the La$^-$ electrons riding the crests (higher density) of the phonon. The holes, M^+, tend to ride the troughs. If they moved as effectively as the electrons there would be no current. The rate of $M^-M^0 \rightarrow M^0M^-$ (electrons moving to the right on the crest of the phonon) is, however, greater than that of $M^+M^0 \rightarrow M^0M^+$ (holes moving to the right on the trough of the phonon) because the exchange integral is smaller for the motion of the hole as a result of the smaller size of M^+ than of M^-, which causes the holes to fall behind the electrons in following the phonons.

For a hyperelectronic metal, such as In ($T_c=3.4$ K, radius 1.550 Å, valence of In^0 3.56, of In$^-$ 2.56, and of In$^+$ 4.56), the electrons ride the troughs and the holes ride the crests.

The compound $\mathrm{La_3In}$ has $T_c=10.4$ K. Because La is hypoelectronic and In is hyperelectronic, I expect electron transfer to take place to the extent allowed by the approximate electroneutrality principle.[13] The unit cube would then consist of 2 La, La$^-$, and In$^+$, with In$^+$ having no need for a metallic orbital and thus having valence 6 with the bonds showing mainly pivoting resonance among the twelve positions. The increase in valence of In and also of La (to $3\frac{1}{3}$) and the assumption of the densely packed *A*15 structure account for the decrease in volume by 14.3%. Because the holes are fixed on the In$^+$ atoms, only the electrons move with the phonon, explaining the increase in T_c.

The mechanism of superconductivity of the copper oxide compounds is different. In its oxides and other compounds, copper has three oxidation states, Cu$^{\mathrm{I}}$, Cu$^{\mathrm{II}}$, and Cu$^{\mathrm{III}}$, the last occurring only rarely. Cu$^{\mathrm{I}}$, in $\mathrm{Cu_2O}$ (cuprite), MCuO (M=Na,K,Rb), $\mathrm{LaCuO_2}$, and other crystals, has 2 O atoms on opposite sides at about 1.85 Å, with 4 or more O atoms at a larger distance. Cu$^{\mathrm{II}}$, in CuO (tenorite), $\mathrm{Cu_4O_3}$ (paramelaconite[14]; linear O—Cu$^{\mathrm{I}}$—O groups are also present), $\mathrm{CaCu_2O_3}$, and other crystals, has 4 O nearby, at about 1.90 Å, with two others more distant. Cu$^{\mathrm{III}}$ is found in $M\mathrm{CuO_2}$ (M=Na,K,Rb,Cs), $\mathrm{LaCuO_3}$, and other crystals to lie at the center of a $\mathrm{CuO_4}$ square with Cu—O bond length of 1.85 Å and with two other O atoms somewhat farther away. The volume per $\mathrm{CuO_6}$ group decreases by two steps of about −10% as the oxidation state of Cu increases from I to III, as is expected for a hyperelectronic element.

Whereas cuprite is red, tenorite is black, showing that there is some electron mobility in this crystal: resonance of $2\mathrm{Cu}^{\mathrm{II}}$ to $\mathrm{Cu}^{\mathrm{I}}+\mathrm{Cu}^{\mathrm{III}}$.

The high-temperature superconductors such as $(\mathrm{Y,La,Sr,Ba})_2\mathrm{CuO}_{4-y}$, with a structure resembling that of K_2NiF_4, differ from other copper-oxygen compounds in that the CuO_4 squares are condensed into infinite layers such that each O lies midway between two Cu. There are thus in the *a* and *b* directions infinite straight lines of alternating Cu and O atoms. I believe that this structure, in interaction with the layers of La and other metals, gives rise to superconductivity.

Cu and O differ in electronegativity by 1.6 units, corresponding to 47% ionic character. Each CuO_4 square, with four covalent bonds about 1.85 Å long, half covalent and half ionic, may be described as involving two pure covalent bonds resonating among the four positions. The bond orbitals of O are essentially 2*p*, with only a small amount of *s* character. The *p* bonds make angles 90° with one another, not 180°. Hence in a sequence $\cdots\mathrm{O—Cu}\cdots\mathrm{O—Cu}\cdots$ there is always an alternation of one pure covalent bond and one "no-bond" (indicated by $\cdots$).

This sequence could be interrupted as an O swings an electron pair to form a bond to one of the four La nearby. Values of the electronegativity of Ba, Sr, La, and Y, 0.9 to 1.0, are so low that these atoms have a positive charge and the O atoms are O^{2-}, with a stable outer octet of electrons. This stability, however, does not prevent the movement of electron pairs along the string of atoms, in synchronism: $\cdots\mathrm{Cu—O}\cdots\mathrm{Cu—O}\cdots\mathrm{Cu—O}\cdots$, the pair of electrons forming the bond on the left side of each O atom moves to the right side, still occupying the same *p* orbital but forming the new bond with its negative lobe.

Anderson pointed out[15] that resonance of covalent bonds in this way would lead to an insulator rather than a substance with metallic conductivity, but he has also stated recently that the doping of La_2CuO_4 with Sr or Ba shifts it away from the insulating state and permits the electron pairs to become superconducting pairs.[16] He describes the mechanism for superconductivity as predominantly electronic and magnetic, although weak phonon interactions may favor the state. I agree with this statement, but point out that other interactions are also involved.

In a line of atoms with an alternation of bonds and no-bonds there are only two structures, each extending the length of the line. The probability of resonance is very small. If, however, some O atoms were missing, so that vacancies interrupted the sequences, there would be the possibility of unsynchronized resonance. Moreover, there is some dismutation of $2\mathrm{Cu}^{\mathrm{II}}$ to $\mathrm{Cu}^{\mathrm{I}}+\mathrm{Cu}^{\mathrm{III}}$. Cu^{I} differs from $\mathrm{Cu}^{\mathrm{III}}$ in having an additional pair, which it can pass on to the next $\mathrm{Cu}^{\mathrm{III}}$ by donating it to the back lobe of a *p* orbital of O as the electron pair occupying the front lobe moves onto the next $\mathrm{Cu}^{\mathrm{III}}$, converting it to Cu^{I}. Somewhat similar processes involving $\mathrm{Cu}^{\mathrm{II}}$ can also occur. If the segments are short enough, the amount of unsynchronized resonance can become so great as to make the conducting state more stable than the insulating state, as is the case with metals. Suitable doping may be required.

Interactions with the La (Ba,Sr) atoms are also essential for high-temperature superconductivity. As in other cases, electron transfer is expected from the hyperelectronic atoms (Cu) to the hypoelectronic atoms (La, Sr,Ba). The distances between La atoms, 3.81 and 3.95 Å, are only a little greater than that in La metal, 3.73 Å. The extra electrons transferred to La from Cu are not required for La—O bonds, because O retains its full complement of 8 electrons in its completed *L* shell. Accordingly these transferred electrons are used in forming covalent bonds that resonate among the La-La and La-Cu positions and confer electronic conductivity on the substance, making it a metal. This conductivity is increased by the resonance along the $\mathrm{O—Cu}\cdots\mathrm{O—Cu}$ lines of atoms, and superconductivity is probably achieved through interaction with a phonon.

Whatever may be the mechanism of superconductivity, it is certain that the value of the critical temperature T_c is increased as the amount of scattering of the electrons by phonons decreases; that is, as the strength of the electron-phonon interaction becomes smaller. The crest-trough theory of this interaction led me years ago to the conclusion that this result could be achieved by combining a crest and a trough superconductor. La (also Sr, Ba, Y, etc.) is a crest superconductor—the extra electron causes tighter binding and greater local density, the phonon crest; whereas Cu would be a trough superconductor—extra electrons would cause a decrease in bonding and in local density.

Tight binding and low atomic weight favor high values of T_c. Sc might accordingly be more effective than Y. I think that no other hyperelectronic element can compete successfully with Cu. Ag and Au have the right oxidation states but are too heavy and too loosely bound. No other hyperelectronic element has a good range of oxidation states.

The observation reported in the press that a green cuprate when heated explodes to give a black powder can be understood. The explosion results from the exothermic release of oxygen to give the metallic oxygen-deficient substance. The release of energy is caused by the extra stability resulting from the increase in valence from electron transfer and the energy of unsynchronized resonance characteristic of metals.

The individual structural features of the high-temperature superconductors are found in other substances. A substance with alternating metal-salt layers is Ag_2F, with sequence $\cdots\mathrm{FAgAgFAgAgF}\cdots$. Resonance between a covalent bond and a no-bond is found in B ($v=3, L=6$) and in metals and organometallic clusters. Hyperelectronic-hypoelectronic electron transfer occurs in many alloys, leading to contraction and increase in the Debye constant. The copper oxide superconductors are the only substances known that incorporate all of these features.

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[1] J. Bardeen, Phys. Rev. **79**, 167 (1950).

[2] H. Fröhlich, Phys. Rev. **79**, 845 (1950).

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957).

[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[5] L. Pauling, Phys. Rev. **54**, 899 (1938).

[6] L. Pauling, Proc. Roy. Soc. London A **196**, 343 (1949).

[7] L. Pauling, J. Solid State Chem. **54**, 2197 (1984).

[8] B. Kamb and L. Pauling, Proc. Nat. Acad. Sci. U.S.A. **82**, 8284 (1985).

[9] L. Pauling and B. Kamb, Proc. Nat. Acad. Sci. U.S.A. **82**, 8286 (1985).

[10] L. Pauling, J. Chem. Soc. **1948**, 1461.

[11] L. Pauling, Proc. Nat. Acad. Sci. U.S.A. **60**, 59 (1968).

[12] L. Pauling and B. Kamb, Proc. Nat. Acad. Sci. U.S.A. **83**, 3569 (1985).

[13] L. Pauling, Proc. Nat. Acad. Sci. U.S.A. **36**, 533 (1950).

[14] M. O'Keeffe and J. O. Bovin, Am. Mineral. **63**, 180 (1978).

[15] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[16] P. W. Anderson, Science **235**, 1196 (1987).