

Chemical nature of the pairing of holes in high-temperature superconductors

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Some crude arguments which point toward a purely electronic (chemical) mechanism for the pairing of p -holes at oxygen are offered. These ideas stem from the fact that reactions of the type (O^- radical) \rightarrow (the peroxide O_2^{--}) \rightarrow (O^{--} ion + O_2 molecule) occur in the gas phase.

Experimental results acquired over the past year could possibly be interpreted as evidence for an oxygen-hole nature of high-temperature superconductivity, according to which the current carriers would be p -holes localized primarily at O^{--} ions. A mechanism of this sort could obviously operate not only in substances having CuO_2 layers but also in compounds which have no copper at all. The magnetic properties would be secondary; in any case, they would not necessarily play a leading role in the pairing process.

This idea was recently formulated clearly by Hirsh.^{1,2} Hirsh also proposed a universal mechanism for the local pairing of p -holes, by virtue of the polarization produced by the pair at one (!) O^{--} ion. In other words, the pairing results from the exchange of a local dipole (primarily electronic) mode. The corresponding equations, written in the Migdal approximation,³ are the same as the results of a recent study by Eliashberg,⁴ who took into account the exchange of several local Einstein (oxygen) modes. I would like to offer some crude, qualitative arguments in support of Hirsh. These arguments are based on the properties of oxygen and its atomic and molecular ions in the gas phase. Clearly, a mechanism of this sort is of a purely electronic (chemical nature).

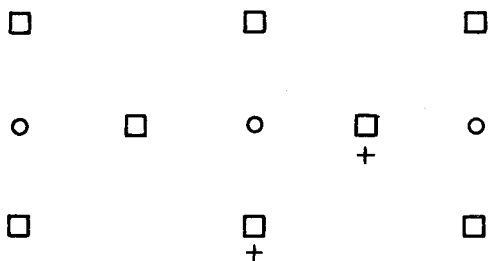


FIG. 1. Here and below, a square represents an $O^{\cdot-}$ ion, and a circle denotes a Cu^{+} ion.

We know quite well that the $O^{\cdot-}$ radical is chemically unstable in a gas, forming the peroxide molecule O_2^- :



Moreover, the peroxide is also unstable at a sufficient gas density:



What do reactions (1) and (2) imply for a solid oxide? (For definiteness, I will speak in terms of CuO_2 layers.) The $O^{\cdot-}$ ion is a normal (ionic) state of oxygen in CuO_2 layers in La_2CuO_4 and $YBa_2Cu_3O_6$. The localization of p -holes at $O^{\cdot-}$ which occurs upon the doping of La_2CuO_4 or in the transition from $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_7$ converts the $O^{\cdot-}$ into the unstable (metallic) radical $O^{\cdot-}$. Reaction (1) is a "Cooper pairing" of holes. The size of the O_2^- "Cooper pair" (in other words, the size of the mobile chemical bond) is accordingly small (Fig. 1), and its energy must of course be estimated at the scale of oxidation-reduction reactions. A factor which lowers the transition temperature is the difference between the size of the peroxide molecule in a gas and that in a solid oxide (a lattice gas).

Reaction (2), which goes at a high hole density, restores the "superconductor" O_2^- to an insulating state, in this instance constituting a lattice of O_2 molecules against the background of the original $O^{\cdot-}$ ions. In "truly neutral" O_2 , all four holes could be said to be on two valence bonds (Fig. 2). A likely alternative in the solid phase might be bound states of four p -holes (of the types in Figs. 3a and 3b) linking O_2 and two $O^{\cdot-}$ ions. Relatively immobile configurations (Figs. 2 and 3) will undoubtedly tend to form a charge density wave.

Phase diagrams including ionic, metallic (superconducting), and charge-density-wave phases have been analyzed from the chemical standpoint by Sleight,⁵ among others. Sleight assumed, however, that the key chemical properties are those of the cations, so that the roles of the insulator $O^{\cdot-}$, O_2 ; the metal $O^{\cdot-}$, O_2 ; and reaction

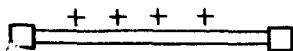


FIG. 2.

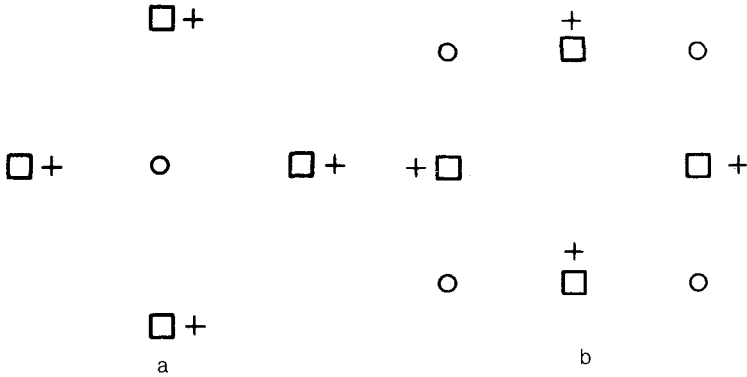


FIG. 3.

(2) in his description were played by, for example, the metal Bi^{4+} ; the insulator Bi^{3+} , Bi^{5+} ; and the disproportionation reaction



That mobile oxygen p -holes of O^- and O_2^- would survive in a significant density in solid oxides in the face of reaction (2) is of course somewhat miraculous. It is evidence of a structural instability, as follows from the well-known argument of Bengt Mathias. However, the calculations in the papers by Hirsh which we have cited inspire faith in this miracle.

¹J. E. Hirsh, "Finite systems studies and the mechanisms of high T_c ," in: Proceedings of the NEC Symposium on Mechanisms of High Temperature Superconductivity, Springer-Verlag, in press, 1988.

²J. E. Hirsh, "Hole superconductivity," UCSD preprint, October, 1988.

³A. B. Migdal, Zh. Eksp. Teor. Fiz. **34**, 1438 (1958) [Sov. Phys. JETP **7**, 996 (1985)].

⁴G. M. Éliashberg, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 275 (1988) [JETP Lett. **48**, 305 (1988)].

⁵A. W. Sleight, "Oxide superconductors: structure-property relationships and mechanisms for high T_c ," in: Superconductivity: Synthesis, Properties and Processing, (ed. W. Hatfield), Marcel Dekker Inc., 1988.

Translated by Dave Parsons