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# **HIGH TEMPERATURE SUPERCONDUCTORS**

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# Hole Superconductivity in Oxides and Other Materials

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## Abstract

A new mechanism that can give rise to superconductivity is discussed. It is proposed that this mechanism, rather than phonons, is the origin of superconductivity in solids.

It has been generally accepted that superconductivity in most solids is due to the electron-phonon interaction.<sup>1,2</sup> This mechanism was proposed in 1950 by Fröhlich<sup>3</sup> and Bardeen<sup>4</sup> and initially supported by measurements of the isotope effect.<sup>5</sup> Posteriorly, the isotope effect was found to vary substantially from one material to another,<sup>6</sup> and the possibility that another mechanism for superconductivity was operative in transition metals and rare earths was seriously considered in the early '60s.<sup>7,8</sup> However, further theoretical work<sup>9,10</sup> and detailed comparison of measured tunneling characteristics with theoretical predictions<sup>11,12</sup> finally seemed to establish that electron-phonon interactions were responsible for superconductivity in all cases known at the time Ref. 1 was written. Other mechanisms for superconductivity involving exchange of "excitons" rather than phonons were proposed in the '60s<sup>13,14</sup> and led to a search for superconductivity in specific structures like quasi-one- and two-dimensional materials. However, no evidence of excitonic superconductivity was found in any material, and until 1986 there was no reason to believe that more than one mechanism was needed to understand superconductivity in all solids.

This comfortable situation, however, was shaken by the discovery of high  $T_c$  superconductivity in oxides.<sup>15,16</sup> It rapidly became clear that electron-phonon interactions were unlikely to account for the phenomenon and many new mechanisms have been proposed for these materials.<sup>16</sup> These include more or less exotic magnetic mechanisms and boson-exchange mechanisms involving various electronic excitations. It seemed inescapable that more than one mechanism was needed to explain superconductivity in solids.

There is another way out, however. There is something very appealing about a single mechanism explaining superconductivity in all solids. In addition, the

properties of the superconducting state in high  $T_c$  oxides do not appear *qualitatively* different from those in the older materials.<sup>17</sup> If electron-phonon interactions cannot do it in oxides perhaps they cannot do it in any material, and there is another universal mechanism that explains superconductivity in all solids.

Why has “excitonic superconductivity” never been found? Surely there are many materials where electronic energy gaps are small enough that such a mechanism would not be too different from an electron-phonon mechanism. We propose the following answer: the direct Coulomb repulsion is just too strong to be overcome by *any* second-order boson exchange process, be it electron-phonon, electron-exciton or electron-plasmon. The one quantity that the conventional theory of superconductivity has most difficulty in dealing with is the Coulomb pseudopotential  $\mu^*$ .<sup>18</sup> It is argued that in transition metals, for example, it is of the order 0.1,<sup>18</sup> but this seems rather unlikely in systems with a large Hubbard  $U$ . A larger  $\mu^*$  can rapidly render the electron-phonon interaction, as well as any other second order process, totally ineffective in giving rise to superconductivity.

Our recent work on oxide superconductors has led us to discover an attractive interaction between electrons that arises from *first order* rather than second order processes.<sup>19–21</sup> Its physical origin is a fundamental asymmetry between electrons and holes in solids. Consider a single band tight binding Hamiltonian for the band originating from an atomic orbital  $\varphi(r)$ <sup>22</sup>:

$$H = \sum_{\substack{(ij) \\ \sigma}} T_{ij} (c_{i\sigma}^+ c_{j\sigma} + h.c.) + \frac{1}{2} \sum_{ijkl} (ij|1/r|k\ell) c_{i\sigma}^+ c_{j\sigma'}^+ c_{\ell\sigma'} c_{k\sigma} \quad (1)$$

with

$$T_{ij} = \int d^3r \varphi_i^*(r) [V(r) - V_{at}^j(r)] \varphi_j(r) \quad (2)$$

$$(ij|1/r|k\ell) = \int d^3r_1 d^3r_2 \varphi_i^*(r_1) \varphi_k(r_1) \frac{e^2}{|r_1 - r_2|} \varphi_j^*(r_2) \varphi_\ell(r_2) \quad (3)$$

with  $V(r)$  the full lattice potential and  $V_{at}^j(r)$  a single atom potential at site  $j$ . The largest contribution to Eq. (2) comes from the part of  $V(r)$  involving the atomic potential at site  $i$ , and we can write:

$$T_{ij} \cong \int d^3r \varphi_i^*(r) V_{at}^i(r) \varphi_j(r) \quad (4)$$

with

$$V_{at}^i(r) = \frac{Ze^2}{|r - R_i|} \quad (5)$$

with  $Z$  the ionic charge. Now let  $\chi_i(r)$  be the wave function for the ion at site  $R_i$ ; as the ion is well localized,  $|\chi_i(r)|^2 \approx \delta(r - R_i)$ . Eq. (4) can then be written as:

$$T_{ij} = - \int d^3r d^3r' \varphi_i^*(r) \varphi_j(r) \frac{Ze^2}{|r - r'|} \chi_i^*(r') \chi_i(r') \quad (6)$$

which is a more fundamental form than Eq. (4).

Now, there is a term in the Coulomb interaction between electrons, Eq. (3), that has precisely this form but involving only electronic wave functions, namely  $(ii|1/r|ji)$ . It is plausible to assume that this term will be *proportional* to  $T_{ij}$  and of opposite sign, and we write:

$$(ii|1/r|ji) = -\alpha T_{ij}. \quad (7)$$

If only nearest neighbor overlaps are important this is of course trivially true. Note that  $\alpha$  defined this way is positive.

The other terms arising from Eq. (3) are:

$$U_{ij} = (ij|1/r|ij), \quad (8)$$

the ordinary Coulomb interaction, and exchange terms

$$\chi_{ij} = (ij|1/r|ji) \quad (9)$$

that are much smaller because they involve the overlap of two wave functions and will be neglected here. Our Hamiltonian becomes, in momentum space:

$$\begin{aligned} H &= \sum_{k\sigma} (\epsilon_k - \mu) c_{k\sigma}^+ c_{k\sigma} - \alpha \sum_{\substack{kk'q \\ \sigma\sigma'}} (\epsilon_k + \epsilon_{k+q}) c_{k+q\sigma}^+ c_{k'-q\sigma'}^+ c_{k'\sigma'} c_{k\sigma} \\ &+ \frac{1}{2} \sum_{\substack{kk'q \\ \sigma\sigma'}} U(q) c_{k+q\sigma}^+ c_{k'-q\sigma'}^+ c_{k'\sigma'} c_{k\sigma}. \end{aligned} \quad (10)$$

The kinetic energy  $\epsilon_k$  is the Fourier transform of  $T_{ij}$ . As  $T_{ij}$  is defined so that  $T_{ii} = 0$ , this implies that  $\epsilon_k$  is defined such that

$$\sum_k \epsilon_k = 0 \quad (11)$$

$U(q)$  is the Fourier transform of  $U_{ij}$ . Redefining the origin of  $\epsilon_k$  would result in redefining  $U(q)$  in Eq. (10) also.

The third term in Eq. (10) is the usual Coulomb repulsion between electrons. The second term is the new effect, that is non-existent in a free electron gas but will always arise in a solid where the electron wave functions are different from plane

waves because of the effect of the lattice potential. This interaction has one essential feature: its sign depends on the kinetic energy, or equivalently on the phases of the wave functions. Near the bottom of the band  $\epsilon_k < 0$  and this interaction is repulsive while near the top of the band  $\epsilon_k > 0$  and it is attractive [recall Eq. (11)].

The pairing interaction in the BCS reduced Hamiltonian obtained from the Hamiltonian Eq. (10) is:

$$V_{kk'} = -2\alpha(\epsilon_k + \epsilon_{k'}) + U(k - k') \quad (12)$$

and we have found that the BCS gap equation

$$\Delta_k = -\frac{1}{N} \sum_{k'} V_{kk'} \Delta_{k'} \frac{1 - 2f(E_{k'})}{2E_{k'}} \quad (13)$$

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2} \quad (14)$$

has solutions for plausible parameters.<sup>21,19</sup> If we neglect the momentum dependence of the repulsive interaction the gap takes the simple form:

$$\Delta_k = \Delta_m \left( -\frac{\epsilon_k}{|\epsilon_m|} + c \right) \quad (15)$$

with  $\Delta_m$  and  $c$  constants.

Equation (13) only has solutions for the Fermi level near the top of the band, as it is in that case where the first term in Eq. (12) becomes most attractive. That is, conduction occurs through holes rather than electrons. The necessary condition for superconductivity is thus that the electrons at the Fermi level are in *antibonding* states. Note that in a “single band solid” a situation where all bonding orbitals are filled and almost all antibonding orbitals are filled would be highly unstable: it is the bonding electrons that bind the solid (hence their name) and the antibonding ones that oppose it.

This model can explain the existence of the isotope effect from the coupling of the phonon degrees of freedom to the second term in Eq. (10).<sup>19</sup> It also provides a simple explanation for the systematic variation in  $T_c$  found in the transition metal series,<sup>19</sup> for high temperature superconductivity in oxides<sup>21</sup> and for the absence of superconductivity in simple and noble metals.

Thus, the essential ingredient of our theory is the realization that holes are different from electrons. At first sight this may appear to violate a fundamental symmetry principle but this is just not so. The symmetry in nature is broken by the fact that electrons and ions have opposite charge, and masses that are not equal but differ by factors of 1000s. There is a deeper symmetry in our discovered asymmetry between electrons and holes: electrons in bonding states lead to *attractive* interactions

between ions and *repulsive* interactions between electrons; electrons in antibonding states (holes) lead to *repulsive* interactions between ions and *attractive* interactions between electrons. The bonding electrons give lattice stability and normal metals, the antibonding electrons give lattice instabilities and superconductors. Both kinds are present in most materials, and their relative weight determines both the stability and the superconductivity.

Thus, our theory exposes the deep underlying reason for the competition found in numerous instances between lattice stability and superconductivity. We expect this mechanism to account for the superconductivity observed in all solids as well as the “transient” superconducting signals observed under metastable conditions such as in CdS,<sup>23</sup> CuCl<sup>24</sup> and metal ammonia solutions<sup>25</sup>: in those instances, rapid quenching presumably freezes the systems in metastable configurations with antibonding states at the Fermi energy. It would be interesting to measure the Hall coefficient in a quenched sample of metal-ammonia solution that displays anomalously low resistivity and verify that it is indeed positive.

We note in closing that Slater<sup>26</sup> has discussed a mechanism for superconductivity that bears some resemblance to the one discussed here, although the crucial role of antibonding states was not recognized at the time.

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## References

1. *Superconductivity*, edited by R.D. Parks (Marcel Dekker, Inc., New York 1969).
2. P.B. Allen. *Nature* **335**, 396 (1988).
3. H. Fröhlich, *Phys. Rev.* **79**, 845 (1950).
4. J. Bardeen, *Phys. Rev.* **79**, 167 (1950).
5. E. Maxwell, *Phys. Rev.* **78**, 477 (1950); C.A. Reynolds et al., *Phys. Rev.* **78**, 487 (1950).
6. See Ref. 2 for a recent review.
7. J. Kondo, *Prog. Theor. Phys.* **29**, 1 (1963).

8. D.C. Hamilton and M.A. Jensen, Phys. Rev. Lett. **11**, 205 (1963); C.G. Kuper, M.A. Jensen and D.C. Hamilton, Phys. Rev. **134**, A15 (1964).
9. J.W. Garland, Phys. Rev. **153**, 460 (1967).
10. G. Gladstone, M.A. Jensen and J.R. Schrieffer, Ref. 1, Chpt. 13.
11. D.J. Scalapino, Ref. 1, Chpt. 10.
12. W.L. McMillan and J.M. Rowell, Ref. 1, Chpt. 11.
13. W.A. Little, Phys. Rev. A **134**, 1416 (1964).
14. V.L. Ginzburg, Sov. Phys. Uspekhi **13**, 335 (1970).
15. J.G. Bednorz and K.A. Muller, Z. Phys. B **64**, 189 (1986).
16. *Proc. Intl. Conf. on High Temperature Superconductors and Materials and Mechanisms of Superconductivity*, Physica C 153-155, 1988.
17. W.A. Little, Science **242**, 1390 (1988).
18. P.B. Allen and B. Mitrovic, Solid State Phys. **37**, 1 (1982).
19. J.E. Hirsch, Phys. Lett. A **134**, 451 (1989); Phys. Lett. A, to be published; UCSD preprint CMT89/02#1.
20. J.E. Hirsch and S. Tang, UCSD preprint, December 1988 and Sol. St. Comm., to be published.
21. J.E. Hirsch and F. Marsiglio, UCSD preprint CMT89/01#1, UCSD preprint CMT89/01#3.
22. J. Hubbard, Proc. Roy. Soc. London **A276**, 238 (1963). We use a tight binding formulation here, although a similar treatment can be given with Wannier functions.
23. G.C.W. Homan et al. Physica B+C **107**, 9 (1982).
24. T.H. Geballe and C.W. Chu, Solid State Phys. **9**, 115 (1979).
25. R.A. Ogg, Phys. Rev. **69**, 243 (1946).
26. J.C. Slater, Phys. Rev. **51**, 195 (1937).