

## Magnon-Exchange Pairing and Superconductivity

A recent suggestion by G. Chen and W. A. Goddard (1) for electron pairing in high-temperature superconducting oxides reintroduced the concept of magnon exchange as a replacement for the standard Bardeen-Cooper-Schrieffer (BCS) phonon exchange (2). This suggestion received considerable attention because [on the basis of microscopic calculations (1, 3) for small clusters] it provided precise estimates of the various superconducting transition temperatures  $T_c$  in the cuprate ceramics and calculated an upper bound  $T_c^{\max} = 232$  K. We show that, within the Chen-Goddard mechanism, the estimates of  $T_c$  are incorrect because Chen and Goddard use an equation for  $T_c$  appropriate only for weak coupling and that their  $T_c^{\max}$  is spurious, as there is no upper bound when the correct expression is used.

The Chen-Goddard calculation makes use of the weak-coupling BCS model (2)

$$T_c = 1.13 T_0 e^{-1/\lambda} \quad (1)$$

where, in the Chen-Goddard mechanism,  $T_0 = |J_{dd}| = 205$  K is a Cu-Cu magnetic exchange parameter, and the dimensionless coupling constant  $\lambda$  is  $(N_0 |J_{pd}|^2)/(2\tau |J_{dd}|)$ . Here  $N_0$  is the band density of states,  $J_{pd}$  is the magnetic coupling of nearest neighbor Cu and O atoms, and  $0 \leq \tau \leq 1$  measures the randomness of the neighboring Cu magnetic moments, with  $\tau = 0$  representing complete randomness. Estimates of the parameters (3) yield  $\lambda$  values of 0.0705  $\tau^{-1}$  for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ , and 0.00609  $\tau^{-1}$  for the chains of  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$ , with  $6.8 \leq \gamma \leq 7$ . For the sheets of  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$ , Chen and Goddard use the parameters from  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  with  $\tau = 0.02$ . With these values, Eq. 1 yields  $T_c = 114$  K and 174 K for  $\tau = 0.05$  and 0.02, respectively. For  $\lambda \rightarrow \infty$ , one obtains  $T_c = T_c^{\max} = 1.13 |J_{dd}| = 232$  K.

McMillan (4) augmented the weak coupling BCS expression in Eq. 1 to include renormalization. This results in the constant prefactor changing from 1.13 to 0.69, and  $\lambda$  being replaced by  $\lambda^* = \lambda/(1 + \lambda)$ . This change, valid for  $\lambda < \sim 1.5$ , is significant when  $\lambda \sim 1$ . For the Chen-Goddard estimate of  $T_c = 114$  K,  $\lambda = 1.41$ . Hence  $\lambda^* = 0.53$  and  $T_c$  becomes 21 K. For the Chen-Goddard estimate of  $T_c = 174$  K,  $\lambda = 3.52$  and the McMillan equation breaks down. It is appropriate, however, to use an expression obtained either as a fit (5) to the

Eliashberg equations or analytically (6), and which gives a reasonable estimate of  $T_c$

$$T_c = a |J_{dd}| (e^{2/\lambda} - 1)^{-1/2} \quad (2)$$

where  $a = 0.25$  gives the correct McMillan limit. For  $\lambda = 3.52$ ,  $T_c = 58$  K.

The estimate of  $T_c^{\max} = 232$  K is a spurious result, derived from the weak coupling expression (Eq. 1). If Eq. 2 is used, at the large  $\lambda$  limit we recover the Allen-Dynes (7) limiting expression  $T_c = 0.18 |J_{dd}| \lambda^{1/2}$ , and  $T_c$  has no upper bound as  $\lambda \rightarrow \infty$ . Within the Chen-Goddard mechanism, estimates of  $T_c$  should be changed from 114 K, 174 K, and 232 K to 21 K, 58 K, and  $\infty$ , respectively.

At this time it is generally accepted that the identity of the exchange boson for the superconducting pairing electrons in the oxides is still an open question. Phonons, excitons, plasmons, and magnons are among the candidates (8), and there are more. In all cases the appearance of a superconducting instability (9) in the original (normal) state has to compete against other, usually energetically more favorable, instabilities. For the magnon exchange mechanism the dominating instability is normally another magnetic phase, for example, ferromagnetism, spiral spin arrangements, or spin glasses.

If the superconducting state is stable in some temperature range, then a  $T_c^{\max}$  may possibly exist if  $\lambda$  in the exponent and the prefactor  $|J_{dd}|$  of Eq. 2 are both renormalized.

It is notoriously difficult to predict the existence of new superconductors and to calculate  $T_c$ , even for conventional electron-phonon coupling (10), because large changes in  $T_c$  are usually found for small changes in coupling. Hence the proposal by Chen and Goddard to test their theory with the use of microscopic electronic calculations of their material parameters is very attractive. However, the cluster calculations of Guo *et al.* (3) give at best rough estimates of the electrical parameters on the scale needed.

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## REFERENCES

1. G. Chen and W. A. Goddard III, *Science* **239**, 899 (1988).
2. J. Bardeen, L. N. Cooper, J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
3. Y. Guo *et al.*, *Science* **239**, 896 (1988).
4. W. A. McMillan, *Phys. Rev.* **167**, 331 (1967).
5. V. Z. Kresin, *Phys. Lett.* **A122**, 434 (1987).
6. L. C. Bourne *et al.*, *Phys. Rev. B Condensed Matter* **36**, 3990 (1987).
7. P. B. Allen and R. C. Dynes, *ibid.* **12**, 905 (1975).
8. S. A. Wolf and V. Z. Kresin, Eds., *Novel Superconductivity in d- and f-Band Metals*, D. H. Douglass, Ed. (American Institute of Physics, New York, 1972), p. 17.
9. M. L. Cohen and P. W. Anderson, in *Superconductivity in d- and f-Band Metals*, D. H. Douglass, Ed. (American Institute of Physics, New York, 1972), p. 17.
10. M. L. Cohen, *Science* **234**, 549 (1986).
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*Response:* Cohen and Falicov's (1) interpretation of our reasoning (2) regarding the maximum achievable  $T_c$  is incorrect. The upper limit for  $T_c$  can be estimated by using the following equation (3)

$$T_c = \frac{\langle \omega \rangle}{1.20} \exp[-1.04(1 + \eta)/\eta] \quad (1)$$

valid for  $\eta \sim 1$ , where in our case

$$\eta = \frac{\lambda N(0)(J_{pd})^2}{8\tau\beta|J_{dd}|} \quad (2)$$

and

$$\langle \omega \rangle = \frac{2}{\eta} \int \alpha^2 F(\omega) d\omega \quad (3)$$

The upper limit of  $\langle \omega \rangle$  is  $4J_{dd}$ , while the upper limit of the exponential term is  $e^{-1}$ , leading to  $T_c < 1.23 |J_{dd}|$ . Our calculated value of  $|J_{dd}| \sim 200$  K leads to  $T_c < 246$  K.

For  $\eta \gg 1$ , the correct formula (3) is  $T_c = 0.18 \sqrt{\langle \omega^2 \rangle} \eta$ , where

$$\langle \omega^2 \rangle = \frac{2}{\eta} \int \alpha^2 F(\omega) d\omega$$

Estimates of the integral in  $\langle \omega^2 \rangle$  using various forms for  $F(\omega)$  lead to  $T_c < |J_{dd}|$ .

Thus the upper limit on  $T_c$  corresponds to parameters such that  $\eta$  is of magnitude one and leads to

$$T_c^{\max} \approx 1.23 |J_{dd}| \approx 246 \text{ K}$$

In our paper (2) we approximated this as

$$T_c^{\max} \approx J_{dd} \approx 200 \text{ K}$$

which we still consider to be a reasonable but conservative estimate.

In our analysis of the maximum  $T_c$  we presume that the values for  $J_{pd}$  and  $J_{dd}$  are constrained within tight limits by the character of the relevant orbitals in the Cu-O sheets (this leads to  $|J_{dd}| \approx 200$  K and  $|J_{pd}| \approx 400$  K, values that increase as the

Cu-O spacing decreases). On the other hand Cohen and Falicov seem to assume that  $|J_{pd}| \rightarrow \infty$  is possible, leading to  $T_c \rightarrow \infty$ .

Given that  $J_{pd}$  and  $J_{dd}$  are fairly tightly constrained, we assume that the variables that may be adjusted (by changing composition, structure, and so forth) to achieve the maximum  $T_c$  are  $\lambda$  (the strength of the coupling, which depends strongly on the concentration of holes in the Cu-O sheets) and  $\tau$  [which depends on the distribution of Cu spins (magnons) for the system with migrating oxygen holes,  $F(\omega)$ ].

There are two alternative approaches to increasing  $T_c$ : (i) increasing  $\lambda$  by increasing the number of holes on the oxygens in the copper-oxygen sheets (this is limited by the overall electrostatic energies that will tend to distribute the holes over the other atoms of the structure) or (ii) decreasing  $\tau$ . [This requires modifying the distribution  $F(\omega)$  to weight lower energy magnons. The migrating oxygen holes of the high  $T_c$  systems have the effect of doing this. However, we cannot yet calculate the  $F(\omega)$  for this complicated dynamic spin system and thus do not have detailed suggestions on how to best decrease  $\tau$ .]

Cohen and Falicov (1) also suggest that the cluster calculations of Guo, Langlois, and Goddard (4) lead to only rough estimates of the parameters. Since the  $T_c^{\text{max}}$  depends sensitively on  $J_{dd}$ , for which there is no direct experimental value (for the systems with Cu-O sheets), we carried out the same type of cluster calculation (generalized valance bond) on the  $K_2NiF_4$  system (same structure as  $La_2CuO_4$ ), where there are direct experimental values of  $J_{dd} = -52$  K and  $-56$  K (5). In this case the calculated value is  $J_{dd} = -51$  K, which suggests that our values for the Cu-O system should be within about 20 K of the calculated 200 K.

There has been a recent experimental estimate made for  $J_{dd}$  of the Cu-O systems. Lyons (6), using Raman light scattering, found an inelastic peak at 0.37 eV for  $La_2Cu_1O_4$  and 0.32 eV for  $Y_1Ba_2Cu_3O_6$  (both semiconductors, not superconductors). As these systems are doped ( $x > 0$ ), this peak rapidly disappears. They interpreted this inelastic transition as a double Cu spin-flip and deduced from linear magnon theory that  $\Delta E = 5.4 J_{dd}$ , leading to  $J_{dd} \sim -790$  K for 2-1-4 and  $J_{dd} \sim -680$  K for 1-2-3. We believe that the large discrepancy with the calculated value argues against this interpretation. We suggest that for the undoped system there may be a small number of oxygen vacancies leading to extra electrons in the system, which would lead to local  $Cu^1$  ( $d^{10}$ ) sites. From similar cluster calculations, we find that the excitation energy  $Cu^1Cu^{II} \rightarrow Cu^{II}Cu^1$  near an oxygen

vacancy is 0.4 eV and suggest that the Raman transition is associated with such  $d^{10} - d^9$  interactions. For the 2-1-4 system, this could be tested directly by experiments at high  $O_2$  pressure that would decrease the number of oxygen vacancy sites and by our suggestion lead to the disappearance of the 0.4-eV peak.

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## Phylogeny and Molecular Data

Biologists with an interest in animal evolution have eagerly looked forward to the results of the new sequencing studies of genetic material, which many colleagues hope will provide "unequivocal phylogenetic trees." Such trees should once and for all solve the problems of homology versus analogy that have perplexed systematists for more than a century.

The recent article, "Molecular phylogeny of the animal kingdom," by Katharine G. Field *et al.* (1) reports the first results of a large investigation of ribosomal RNA from a number of phyla and illustrates the results with four evolutionary trees resulting from analyses of four slightly different selections of sequences.

Unfortunately, the four trees show four different branching relationships of echinoderms, annelids, arthropods, and chordates. The tree illustrating the more detailed relationships of some mollusks (a nudibranch, two clams, and a chiton), two annelids (a polychaete and an oligochaete), a pogonophoran, a sipunculid, and a brachiopod shows the brachiopod and the polychaete as sister groups derived from chitons and the earthworm as derived from another point within the mollusks. This will appear unacceptable to most systematists.

As the authors also state, analyses of additional portions of the RNA molecule will establish the branching orders with higher probability, but it is important to point out that the molecular data do *not* provide unequivocal phylogenetic trees and must be treated with just as much criticism, care, and tact as the traditional morphological characters.

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## REFERENCES AND NOTES

1. M. L. Cohen and L. M. Falicov, *Science* **243**, 547 (1989).
  2. G. Chen and W. A. Goddard III, *ibid.* **239**, 899 (1988).
  3. P. B. Allen and R. C. Dynes, *Phys. Rev. B* **12**, 905 (1975).
  4. Y. Guo, J.-M. Langlois, W. A. Goddard III, *Science* **239**, 896 (1988).
  5. R. J. Birgeneau, J. Als-Nielsen, G. Shirane, *Phys. Rev. B* **16**, 280 (1977); R. J. Birgenneau, J. Skalyo, G. Shirane, *J. Appl. Phys.* **41**, 1303 (1970). The  $J$  in this paper is defined to be twice as big as in our convention.
  6. K. B. Lyons *et al.*, *Phys. Rev. B* **37**, 2353 (1988); K. B. Lyons *et al.*, *Phys. Rev. Lett.* **60**, 732 (1988). The  $J$  in this paper is defined to be twice as big as in our convention.
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## REFERENCE

1. K. G. Field *et al.*, *Science* **239**, 748 (1988).  
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Perhaps the most striking and unexpected result of the investigation into metazoan phylogeny with 18S ribosomal RNA (rRNA) partial sequences, as reported by Field *et al.* (1), is the indication that the two sequences from Cnidaria (a hydra and a sea anemone) branch from a lineage including ciliates, fungi, and higher plants. They suggest that this provides strong evidence that the Cnidaria arose independently from other metazoan groups. However, they do not mention that this analysis contradicts the implication of 5S rRNA sequence data from a variety of Cnidaria. All the cnidarian 5S rRNA sequences clearly cluster with those of all other known metazoan 5S rRNA sequences, from a great variety of metazoans (2). The 5S rRNA sequence from a sponge also clearly clusters with that of metazoan sequences (2), although no 18S rRNA data from sponges are given by Field *et al.* On the basis of morphological simplicity, the relatedness of sponges to other metazoans has been more frequently questioned than that of Cnidaria (3). Even the 5S rRNA sequence from the primitively multicellular mesozoan *Dicyema misakiense* suggests probable branching from the metazoan lineage at an early stage (4, 5). The 5S and 18S rRNA data are in agreement in suggesting that the sequences from the planarian *Dugesia* represent the most isolated metazoan lineage (1, 2). The admittedly incomplete and controversial fossil record suggests a nearly simultaneous initial radiation of lineages representing Cnidaria and a variety of other metazoans, 600 to 700 million years ago (6). This is consistent with the 5S rRNA