Linear Electron–Hole–Electron Pair Model of High-Temperature Superconductivity in $La_{2-x}M_xCuO_4$ and $LBa_2Cu_3O_{7-y}$. Small Cooper Pair Formation in Linear Cu^{2+}-O-Cu^{3+}-O-Cu^{2+} Units via Concerted Breathing-Mode Vibration

Sir:

Current carriers of conventional Bardeen–Cooper–Schrieffer (BCS) superconductors are pairs of electrons,[1] which arise from electron–phonon interactions: A moving electron induces a slight, momentary lattice deformation around it, which affects the movement of a second electron in the wake of the first in such a way that, effectively, the two electrons move as an entity (i.e., a Cooper pair) as if bound together by an attractive force. Whether or not these interactions are also responsible for the electron pairing of the high-temperature superconductors $La_{2-x}M_xCuO_4$ (M = Ba, Sr; $x \cong 0.15$; superconducting transition temperature $T_c \cong 35$ K) and $LBa_2Cu_3O_{7-y}$ (L = Y, Sm, Eu, Gd, Dy, Ho, Yb; $y < 0.3$; $T_c \cong 93$ K) has been a controversial subject.[2,3] Recently, an increasing number of experimental studies suggest that phonons do play an important role in the electron pairing of the copper oxide superconductors: (a) For both $La_{1.85}Sr_{0.15}CuO_4$[4a,c] and $YBa_2Cu_3O_{7-y}$,[4b,c] small but significant oxygen isotope effects are found. (b) According to Mössbauer studies[5] on ^{151}Eu- and ^{119}Sn-doped $EuBa_2Cu_3O_{7-y}$, a softening of copper–oxygen vibrational modes occurs as a precursor to the onset of superconductivity. (c) The thermal conductivity of $YBa_2Cu_3O_{7-y}$ increases sharply below T_c,[6a] due most likely to a drastic reduction in the phonon scattering by holes (i.e., formal Cu^{3+} centers) as holes form superconducting pairs. The thermal conductivity of $La_{1.8}Sr_{0.2}CuO_4$ also exhibits a small upturn below its T_c.[6b] (d) A far-infrared study[7] of $YBa_2Cu_3O_{7-y}$ shows narrowing of phonon lines at 155 and 195 cm^{-1} in the superconducting state, in analogy with the effect of the electron–phonon interaction in conventional BCS superconductors.

Thus, a correct electron-pairing mechanism for the copper oxide superconductors must incorporate electron–phonon interactions in some way. Cooper pairs of conventional BCS superconductors are large (coherence length of $\sim 10^4$ Å), so that many pairs ($\sim 10^6$) overlap within the volume of one pair ($\sim 10^{12}$ Å^3), thereby leading to a long-range order.[8] Cooper pairs of the copper oxide superconductors are estimated to be very small (coherence length of ~ 12 Å),[3e] so that one needs to understand how such small pairs give rise to a long-range order. On the basis of the analysis of how the T_c value and the overall Cu2–O4–Cu1–O4–Cu2 linkage distance of $YBa_2Cu_3O_{7-y}$ vary as a function of the oxygen content, it was suggested[9] that the 93 K superconductivity might involve Cooper pair formation across the Cu2–O4–Cu1–O4–Cu2 linkages (See Figure 1 of ref 10), which connect the copper atoms of one CuO_2 layer to those of the other CuO_2 layer in each superconducting $Ba_2Cu_3O_{7-y}{}^{3-}$ slab. These linkages are about 8 Å long, which is comparable to the coherence length of the Cooper pair (~ 12 Å).[3e] On the basis of band electronic structure calculations,[9b,10,11] we may describe the Cu2–O4–Cu1–O4–Cu2 linkage by the electron configuration ϕ_1 (i.e., Cu^{2+}–O^{2-}–Cu^{3+}–O^{2-}–Cu^{2+} in **1**). The tendency for Cu^{2+} ions to disproportionate into Cu^+ and low-spin Cu^{3+} ions[12] makes the configuration ϕ_2 (i.e., Cu^{3+}–O^{2-}–Cu^+–O^{2-}–Cu^{3+} in **1**) also appropriate for the linkage. Promotion of electrons from the oxygen p-block to the copper d-block levels[13] in ϕ_2 leads to the configuration ϕ_3 (i.e., Cu^{2+}–O^-–Cu^+–O^-–Cu^{2+} in **1**), in which the promotion energy is in part compensated by the removal of the on-site repulsion on an oxygen atom. In general, the electronic structure of a Cu2–O4–Cu1–O4–Cu2 linkage or any other linear Cu^{2+}–O^{2-}–Cu^{3+}–O^{2-}–Cu^{2+} unit in the CuO_2 layers is best described by the linear combination $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$.[14] Lack of evidence for Cu^{3+} ions in the copper oxide superconductors as determined from spectroscopic studies[15] might arise from the participation of a configuration such as ϕ_3.

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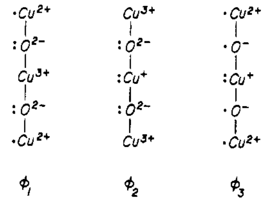

The concerted breathing-type distortion **2a** favors ϕ_1, while **2b** favors ϕ_2 and ϕ_3. (Here **2a** and **2b** refer to Cu^{2+}–O^{2-}–Cu^{3+}–O^{2-}–Cu^{2+} units of the CuO_2 layers. Similar breathing-mode distortions can be considered for the Cu2–O4–Cu1–O4–Cu2 linkages.) Thus, the weight of ϕ_1 in ψ would be greater in **2a** than in **2b**, while the weight of ϕ_2 or ϕ_3 would have an opposite trend. In a sense, the distortion **2a** → **2b** forces the two electrons at the

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(13) Here the oxygen p- and copper d-block levels refer to *interacted levels* that have copper–oxygen bonding and antibonding characters, respectively, as discussed in ref. 9b.

(14) (a) In ϕ_1 the two spins are assumed to be paired. The configurations ϕ_2 and ϕ_3 are extremes. Other configurations may well contribute to the expansion of ψ, which will not alter the basic tenets of the present argument. (b) For configuration interactions in a mixed-valence system as a function of geometry relaxation, see: Shaik, S. S.; Whangbo, M.-H. *Inorg. Chem.* **1986**, *25*, 1201.

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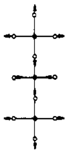

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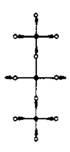

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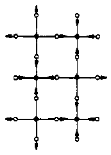

3

end copper atoms of a Cu^{2+}–O–Cu^{3+}–O–Cu^{2+} unit to flow into the middle copper atom to make a Cu^{3+}–O–Cu^{+}–O–Cu^{3+} unit, whereas the distortion **2b** → **2a** leads to the opposite valence fluctuation. Effectively, the mixed-valence fluctuation in a linear Cu^{2+}–O–Cu^{3+}–O–Cu^{2+} unit induced by a concerted breathing-mode vibration such as **2a** ↔ **2b** can serve as an electron-pairing mechanism: As illustrated in **3**, a concerted breathing-mode distortion (**2a**) at a given Cu^{2+}–O–Cu^{3+}–O–Cu^{2+} unit is likely to induce a concerted breathing-mode distortion of opposite parity (**2b**) on the nearest-neighbor Cu^{2+}–O–Cu^{3+}–O–Cu^{2+} units. Thus, a long-range order in the entire lattice can be achieved by successively inducing concerted breathing-mode vibrations of opposite parity between all nearest-neighbor Cu^{2+}–O–Cu^{x+}–O–Cu^{2+} (x = 2, 3) units. Then two electrons "confined" in each Cu^{2+}–O–Cu^{3+}–O–Cu^{2+} unit would move effectively as an entity rather than act independently, since the latter would require energy to break a series of successive concerted breathing-mode vibrations.

Two electrons involved in the valence fluctuation of a linear Cu^{2+}–O–Cu^{3+}–O–Cu^{2+} unit via its concerted breathing-mode vibration may be referred to as a linear electron–hole–electron (e–h–e) pair. Evidence for a breathing-mode vibration has recently been found for $La_{2-x}M_xCuO_4$ from electron diffraction measurements,[16] so that the concerted breathing-mode vibration invoked for linear e–h–e pairing seems reasonable. $LBa_2Cu_3O_{7-y}$ is expected to contain holes both in the CuO_2 layers and in the CuO_3 chains (vide infra), so that linear e–h–e pairing can occur in the layers and the Cu2–O4–Cu1–O4–Cu2 linkages. The latter is compatible with the finding from a Mössbauer study[5b] that the Cu1–O vibrational modes undergo a softening as a precursor to the superconductivity onset and also with the observation from a ^{63}Cu nuclear spin-relaxation study[17] that the Cu1 atoms are also involved in electron pairing.

According to the linear e–h–e pair model, atoms involved in the pairing must undergo concerted breathing-mode vibrations. However, atoms not involved in the pairing are not constrained in their vibrational modes and hence may engage in certain modes that disrupt linear e–h–e pairing. Such pair-breaking vibrations are generally suppressed by lowering the temperature of a crystal lattice. If more holes are present in the lattice, more atoms are involved in linear e–h–e pairing, and fewer atoms remain to provide pair-breaking vibrational modes. Consequently, a crystal with more holes requires less cooling to suppress the pair-breaking vibrational effect, thereby leading to a higher T_c value. This accounts for why the T_c values of $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ are observed to increase almost linearly with the number of holes.[18]

The CuO_4 layers of $La_{2-x}M_xCuO_4$ are made up of axially elongated CuO_6 octahedra by sharing their equatorial oxygen atoms (O_{eq}). The axial oxygen atoms (O_{ax}) of each CuO_6 octahedron have short contacts with La^{3+} cations (and with M^{2+} cations at the La^{3+} sites as well) along the Cu–O_{ax} direction to form La⋯O_{ax}–Cu units perpendicular to the $Cu(O_{eq})_2$ plane.[19] In $La_{2-x}M_xCuO_4$ an applied pressure is expected to exert its strongest effect along the direction perpendicular to the CuO_4 layers. In particular, an applied pressure along the La⋯O_{ax}–Cu units will suppress the vibrational modes arising from the Cu–O_{ax} stretching. Only the concerted breathing-mode vibrations associated with the $Cu(O_{eq})_2$ planes are essential for linear e–h–e pairing, and hence the vibrational modes of the Cu–O_{ax} stretching will disrupt linear e–h–e pairing. Since this pair-disrupting effect can be suppressed by an applied pressure, the T_c value of $La_{2-x}M_xCuO_4$ increases substantially with an applied pressure (dT_c/dp = 0.64 K/kbar).[20]

Let us now consider the origin of the plateaus in the T_c vs oxygen content plot of $YBa_2Cu_3O_{7-y}$ ($T_c \cong 93$ K for $y \cong 0.15$–0.25; $T_c \cong 55$ K for $y \cong 0.4$–0.5).[9,21] The distance of the Cu2–O4–Cu1–O4–Cu2 linkage increases with increasing y,[9] which is unfavorable for linear e–h–e pairing to occur in the linkage even if a hole is present in it. Thus, the lower plateau at $T_c \cong 55$ K would mean that linear e–h–e pairing occurs only within the CuO_2 layers.[9] Therefore, one experimental test for the linear e–h–e pair model would be to perform ^{63}Cu nuclear spin-relaxation measurements on $YBa_2Cu_3O_{7-y}$ of the lower plateau region (i.e., $T_c \cong 55$ K for $y \cong 0.4$–0.5),[9,21] for which only one pairing energy associated with the copper atoms of the layers is expected. Within the linear e–h–e pair model, the observation of the nearly constant T_c, which defines each plateau region, implies that the number of holes does not significantly change for the range of y values in that region. According to the electronic structure studies on $YBa_2Cu_3O_{7-y}$,[9] the oxidation state of Cu1 is Cu^{3+} when the Cu1 site is planar four-coordinate but Cu^{+} in all other cases. The $YBa_2Cu_3O_{7-y}$ lattice gains two electrons when an O1 atom is removed from the CuO_3 chains. Thus, removal of a bridging O1 atom between two planar four-coordinate Cu1 sites destroys *two holes* in the CuO_3 chain but creates *two holes* in the CuO_2 layers. Removal of a bridging O1 atom between planar three- and four-coordinate Cu1 sites destroys one hole in the CuO_3 chain and hence does not change the number of holes in the CuO_2 layers. This explains how the number of holes in the whole $YBa_2Cu_3O_{7-y}$ lattice or that in the CuO_2 layers can remain unchanged for a range of different y values. For large values of y, removal of an oxygen atom is likely to occur from a bridging O1 site between two three-coordinate Cu1 atoms. Since the removal does not change the number of holes in the CuO_3 chain, two holes in the CuO_2 layers are destroyed. The CuO_2 layers can be free of holes (i.e., consist of only Cu^{2+} sites) if the numbers of Cu^{3+} and Cu^{+} sites in the CuO_3 chains maintain the ratio $(1 - y)/y$.[9a] This accounts for the nonsuperconducting, semiconducting, and antiferromagnetic properties of $YBa_2Cu_3O_{7-y}$ for $y > 0.5$.[9a,22]

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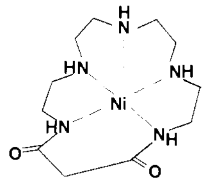
Ni^{II}(dioxo[16]aneN_5)-Induced Methane Formation from Methyl Coenzyme M

Sir:

The nickel tetrapyrrole containing factor, F_{430}, is implicated in the final methane evolution step in methanogenic bacteria[1-4] and has attracted considerable attention.[5-8] The essential role of F_{430} in methane formation was demonstrated by Ankel-Fuchs and Thauer, who reported the in vitro catalysis of $H_3CSCH_2CH_2SO_3^-$, methyl coenzyme M (methyl-CoM), to methane and CoM by purified methyl-CoM reductase under reducing conditions.[9] Since F_{430} exists in both the Ni(I) (or Ni(III)) and the Ni(II) states in *Methanobacterium thermoautotrophicum*,[10,11] it is of interest to examine the role of the nickel ion oxidation state[12,13] in methyl-CoM catalysis. We have found both the mono- and the divalent oxidation states of the water-soluble Ni(dioxo[16]aneN_5), NiL, complex[14] catalyze methyl-CoM to methane and CoM.



$Ni^{II}L$

In a typical reaction $Ni^{II}L$ (0.267 mM) in deoxygenated distilled H_2O (20 mL) was placed into a two-neck round-bottom flask equipped with a magnetic stirbar. Methyl-CoM[15] (0.800 mM) was added under a heavy flow of argon and the flask connected to a gas-uptake manometer.[16] Methane was identified as the sole carbon-containing gas phase product by GC, IR, and MS analysis,[17] and the extent of product formation was assayed either by the gas-uptake manometer or by the integration of the methyl and ethylene ^1H NMR signals of the methyl-CoM and CoM containing final reaction mixture.[18] One equivalent of methyl-CoM per equivalent of $Ni^{II}L$ forms 0.60 ± 0.04 equiv of CoM and 0.20 ± 0.02 equiv of 2,2′-dithiobis(ethanesulfonic acid), CoM disulfide.[15] As the reaction proceeds, the green solution containing $Ni^{II}L$ and methyl-CoM becomes brown with an UV-visible spectrum identical with that of $Ni^{II}L$ titrated with CoM (Figure 1).[19] Since the reaction continues until 1.2 ± 0.1 equiv of methyl-CoM is consumed, it is evident the formation of Ni-CoM prevents additional conversion of methyl-CoM. The fact that no methane is produced when methyl-CoM is added to a solution containing an equimolar amount of $Ni^{II}L$ and CoM supports this conclusion.

The magnetic susceptibility of the reaction mixture was measured by the Evans method.[20] $Ni^{II}L$ ($\mu = 2.60\ \mu_B$) and methyl-CoM were placed in a concentric NMR tube and sealed under argon. As 1 equiv of methyl-CoM was consumed during the reaction, the magnetic susceptibility slowly increased to a final value of 2.74 μ_B. This small increase in the magnetic moment is attributed to the formation of Ni^{II}(L)(CoM).[19] When the reaction is run under O_2, the magnetic moment per nickel increased from 2.99 to 3.17 μ_B.[20]

We do not believe that $Ni^{I}L$ is required for methane evolution for the following reasons. In the presence of an 8:1 excess of substrate to $Ni^{II}L$ at 21.5 ± 1 °C the initial rate is $(1.94 \pm 0.14) \times 10^{-2}$ (mol of CH_4) (mol of Ni)$^{-1}$ h^{-1} under 1 atm of argon and $(2.24 \pm 0.16) \times 10^{-2}$ (mol of CH_4) (mol of Ni)$^{-1}$ h^{-1} under 1 atm of O_2.[21] It is expected that O_2 would inhibit the formation of

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(14) Kimura, E.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1984**, *106*, 5497. Dioxo[16]aneN_5 (L) ^1H NMR ($CDCl_3$): δ(TMS) 7.90 (s, 2 H, amide), 3.30 (m, 4 H, amide ethylene), 3.20 (s, 2 H, malonyl methylene), 2.85 (m, 12 H, ethylene), 2.00 (b s, 3 H, amine). ^{13}C NMR ($CDCl_3$): δ(TMS) 169.0, 49.0, 48.5, 48.0, 43.0, 38.5. The UV-vis spectrum of $Ni^{II}L$ is pH-dependent. UV-vis [pH 9.5 borate buffer] (ε): 260, 290 (1664), 340 nm (120).

(15) For the preparation of methyl-CoM see: Taylor, C. D.; Wolfe, R. S. *Biochemistry* **1978**, *17*, 2374. Sodium salt of 2-mercaptoethanesulfonic acid (CoM) ^1H NMR (D_2O): δ(TMS) 2.97 (m, 2 H), 2.67 (m, 2 H). Ammonium 2-(methylthio)ethanesulfonate (NH_4(methyl-CoM)) ^1H NMR (D_2O): δ(TMS) 2.99 (m, 2 H), 2.69 (m, 2 H), 1.95 (s, 3 H). The disodium salt of 2,2′-dithiobis(ethanesulfonic acid) (CoM disulfide) was prepared by titrating an aqueous solution of CoM with I_2 until its color persisted. ^1H NMR (D_2O): δ(TMS) 3.13 (m, 4 H), 2.88 (m, 4 H). Methyl-CoM does not decompose to methane and CoM between pH 4 and pH 9.5.

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(18) After a reaction was complete, the solution was freeze-dried and reconstituted with D_2O. ^1H NMR integration of CoM and methyl-CoM was within ±4% of the yield of methane gas evolution calculated according to step 6. No carbon-containing side products were observed in the GC, GC-MS, ^1H NMR, or FT-IR measurements in either the gas or the solution phase. The background O_2 concentration observed in the GC-MS spectrum of the gas-phase products introduced significant uncertainty in the determination of [O_2].

(19) When LNi^{II} was titrated with CoM, new UV-visible absorptions in a pH 9.5 borate buffer were observed (ε): 333 (2217), 405 (754), 510 nm (297).

(20) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Becker, E. D. *High Resolution NMR: Theory and Chemical Applications*, 2nd ed.; Academic: New York, 1980; pp 42-61. (c) Shifts are based on *tert*-butyl alcohol. The reproducibility between samples is about ±0.15 μ_B, but the magnitude of the magnetic susceptibility increase during each run is reproducible within ±0.02 μ_B. Magnetic susceptibility measurements were taken every $^1/_2$ h for the initial 4 h and every 4 h thereafter.

(21) The rate of LNi^{II} decomposition under O_2 is slow compared to the initial rate.

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