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Predicted properties of $Nd_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ and related high-temperature superconductors

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The charge-reservoir oxygen model of superconductivity predicts a critical temperature of $T_c \approx 30$ K for $R_{1.5}Ce_{0.5}Sr_2Cu_2MO_{10}$ ($R222M$-10) (with R = Eu, Sm, and Nd, and M = Ta and Nb), in agreement with the measured values ≈28 K. The model also successfully predicts $RBa_2Cu_2MO_8$ ($R122M$-8) to be an insulator. Other predictions for $R222M$-10 in need of testing are (i) it is a p-type superconductor; (ii) the superconductivity originates primarily in the Sr-O layers, not in the cuprate-planes; (iii) on cuprate-plane Cu sites, of order ~1% Ni should depress T_c to zero, while about six times as much Zn will be required to destroy superconductivity; (iv) magnetic impurities on Cu sites and Sr sites, but not rare-earth sites, will break Cooper pairs; (v) Pr on Sr sites will suppress T_c; (vi) the failure of $Pr_{1.5}Ce_{0.5}Sr_2Cu_2MO_{10}$ to superconduct is due to the antistructure defect (Pr_{Sr}^{+3},Sr_{Pr}^{+2}); (vii) T_c is small because the primary superconducting condensate in the charge-reservoir Sr-O layers is only ≈2 Å from the cuprate-planes; and (viii) the superconductivity should disappear with heavy Ce doping ($z \rightarrow 1$) in $R_{2-z}Ce_zSr_2Cu_2MO_{10}$. The relationships of $R222M$-10 to $R122M$-8, $RBa_2Cu_3O_7$, and $R_{2-z}Ce_zCuO_4$ are discussed. [S0163-1829(98)10517-9]

I. INTRODUCTION

The class of superconductors $R_{2-z}Ce_zSr_2Cu_2MO_{10}$ with $z \approx 0.5$ ($R222M$-10) for M = Ta and Nb, are materials which superconduct for the rare-earth ions R = Eu, Sm, Nd, and Gd (with $T_c \approx 28$ K), but not for R = Pr.[1–11] Here we take $Nd_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ to be the prototype of these compounds.

These materials fit into a sequence that is particularly interesting, which includes the materials (i) $RBa_2Cu_3O_7$ ($R123$-7),[12] (ii) $RBa_2Cu_2MO_8$ ($R122M$-8), (iii) $R222M$-10, and (iv) $R_{2-z}Ce_zCuO_4$ with $z \approx 0.15$ ($R21$-4). They all have similar crystal structures: $R123$-7 has the well-known $NdBa_2Cu_3O_7$ crystal structure of Fig. 1(a) with a rare-earth ion R at the center of the unit cell, slightly crinkled CuO_2 cuprate-planes on either side, sandwiched by Ba-O layers, which in turn are sandwiched between Cu-O chain layers (each of which is only half within the unit cell). The crystal structure of $R122M$-8 is given in Fig. 1(b), and is the same as for $R123$-7 except that the Cu in the Cu-O chains has been replaced by M = Nb or Ta, and the previously empty antichain sites between the M ions in that layer have been occupied by oxygen ions. $R222M$-10 [Fig. 1(c)] is obtained by replacing Ba by isoelectronic Sr,[13] slicing the crystal structure of $R122M$-8 perpendicular to the c-axis at the R layer, moving the two halves of the unit cell apart, replacing each half-R by an entire R ion (now Ce-doped, as in $Nd_{0.75}Ce_{0.25}$), inserting an O_2 layer in between, and displacing the upper part in the **a** and **b** directions so that Sr in the upper portion is directly above a cuprate-plane Cu in the lower portion. Finally $R21$-4 [Fig. 1(d)] results when the $SrO/MO_2/SrO/CuO_2$ layers are removed from $R222M$-10 and the Ce content per R ion reduced to 0.075 so that we have $z \approx 0.15$: $Nd_{0.925}Ce_{0.075}$.

These materials offer an especially appropriate proving ground for theories which purport to offer explanations of high-temperature superconductivity, because they provide clear chemical trends in their crystal structures, because $R222M$-10 has been studied sufficiently little that many of its properties are unmeasured (providing an opportunity for the theorists to make genuine *predictions*), and because they behave very differently: (i) $R123$-7 is a ≈90 K superconductor for most rare-earth ions,[14] including R = Pr,[15–22] but with the notable (current) exceptions R = Ce and Cm being larger-radius magnetic ions that are likely to occupy Ba sites in significant quantities, where they would break Cooper pairs and destroy superconductivity if the primary supercurrent were in the charge-reservoir Cu-O chain layers[23]; (ii) in contrast, $R122M$-8 is an insulator for the rare-earth ions studied to date,[3] (iii) $R222M$-10 is a superconductor at ≈28 K, for R = Nd, Sm, Eu, and Gd, but not for R = Pr, which is an insulator,[9] and (iv) $R21$-4 is typically a $T_c \approx 21-24$ K superconductor with Ce doping, for R = Pr, Nd, Sm, and Eu, with T_c ranging from ≈9 K for R = Eu, to 24.3 K for R = Pr (carefully prepared),[24] to 32 K for R = Nd (pressure fabricated);[25] but $R21$-4 does not superconduct for R = Gd and trivalent rare-earth ions smaller than Gd^{+3}.[25–30] There are indications[30] that $Y_{2-z}Ce_zCuO_4$, if it could be fabricated, would not superconduct. Moreover, since growth under pressure causes $Nd_{2-z}Ce_zCuO_4$ to superconduct at 32 K,[25] we think that such pressure-growth might produce $Eu_{2-z}Ce_zCuO_4$ with a critical temperature T_c higher than the current ≈9 K.

Ca-doped $Tm_{2-z}Ca_zCuO_4$ superconducts with $T_c \approx 30$ K, but neither Ce doping nor superconductivity has been demonstrated for R_2CuO_4 compounds with trivalent rare-earths whose radii are smaller than Gd's.[31] Yet T_c ranges from 19

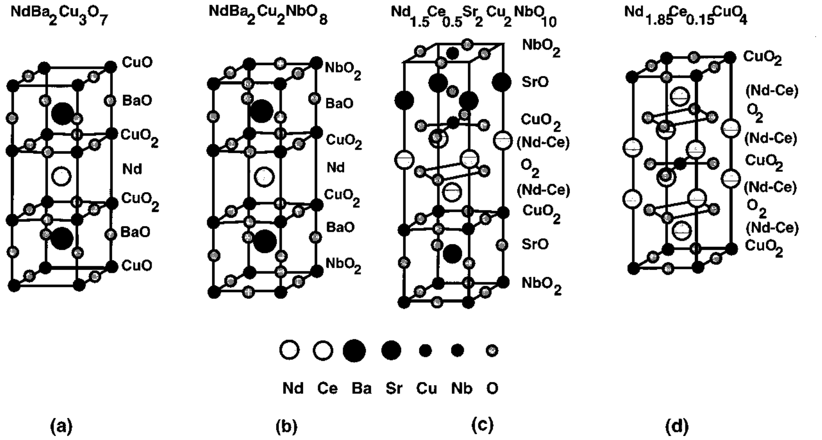

FIG. 1. Crystal structures showing (a) a unit cell of Nd123-7, (b) a unit cell of Nd122M-8, (c) a formula unit (half-cell) of $Nd_{1.5}Ce_{0.5}Sr_2Cu_2M$-$O_{10}$, and (d) a unit cell of $Nd_{1.85}Ce_{0.15}CuO_4$.

K to 21 K for $La_{1-x}Nd_xCe_{0.15}CuO_4$ with $0 \leqslant x \leqslant 0.85$,[29] but $LaGd_{0.8}Ce_{0.2}CuO_4$ does not superconduct.[32]

II. CHARGE-RESERVOIR OXYGEN MODEL

First we attempt to understand the observed chemical trends using the charge-reservoir oxygen model of superconductivity[33–36] in cuprate superconductors.

A. Prediction of which materials superconduct

In the charge-reservoir oxygen model, the superconductivity occurs at $T_c \approx 90$ K for all R123-7 homologues, and is primarily associated with the charge-reservoir layers of the crystal structure, where oxygen supplies holes for p-type conduction and superconduction: namely, in the vicinity[37] of the Cu-O chain layers in R123-7. The cations Ba and Cu can assume, at most, the (integral) charge-states Ba^{+2} and Cu^{+2}. The rare-earths are R^{+3} (Tables I and II[38–40]), leaving a total of 13 electrons to charge the 7 oxygen anions: Based on ionization potential data[40] and Madelung potential calculations[27,41] such as those in Table I, the first of the cations to be further ionized would be $Cu^{+2} \rightarrow Cu^{+3}$, but nuclear magnetic resonance (NMR) data show that there is no Cu^{+3} in $YBa_2Cu_3O_7$ (and presumably there is none in Nd123-7 either),[42] and point-ion-model calculations show that none of the Cu sites has a Madelung potential as large as the $Cu^{+2} \rightarrow Cu^{+3}$ ionization potential. Indeed, the Madelung potential is too small in magnitude by at least ~10 V. (See Table I.) Therefore a maximum of 13 electrons can charge at most 6.5 oxygen anions to $\approx -2|e|$, leaving (in some sense) $\approx 0.5\ O^0$ or $\approx 1.0\ O^{-1}$ in each unit cell: hypocharged oxygen, O^{-Z}, with $Z<2$. In this model, the onset of superconductivity in $YBa_2Cu_3O_x$ and its homologues is associated with the initial formation of hypocharged or ''neutral'' oxygen: $x \approx 6.5$.[23,34,43] Hypocharged oxygen also accounts for the threshold of superconductivity in $Y(Ba_{1-y}La_y)_2Cu_3O_x$, where the Tokura-Torrance Rule[43,44] for the phase boundary between insulating and superconducting materials, $x=6.5+2y$, is an almost trivial consequence of the oxygen model.[43] Therefore, in this model, hypocharged oxygen is

TABLE I. Sites in Nd123-7 and the charges on those sites (in units of $|e|$), as extracted from neutron diffraction data,[38] using the bond-valence-sum method.[39] Also displayed are the corresponding Madelung potentials (in V), calculated in a point-ion model, and some ionization potentials.[40] The parentheses enclose the final charge state of the ionization. The results for $Z=0$ correspond to the ideal crystal; $Z=1$ corresponds to two Nd ions of charge $Z|e|$ greater than the charge of Ba, on Ba sites in the central unit cell, together with an antisite oxygen of charge $-2Z|e|$. This table indicates that the ions should have the following charge states on their normal sites: Nd^{+3}, Ba^{+2}, and Cu^{+2}. Ba-site Nd should be Nd^{+2} for $Z=0$, but Nd^{+3} if oxygen simultaneously occupies the antichain site $(Z=1)$. The charge of the hypocharged oxygen is emboldened.

		Madelung potentials			
Site	Charge	$Z=0$	$Z=1$	Ionization potentials	
Nd	3.05	−28.59	−27.58	22.1(+3)	40.4(+4)
Ba	2.13	−17.15	−23.77	10.0(+2)	
Cu(1) Cu-O chain layer	2.21	−23.82	−30.27	20.3(+2)	36.3(+3)
Cu(2) CuO_2 plane layer	2.06	−25.95	−25.91	20.3(+2)	36.3(+3)
O(1) (Cu-O chain layer)	**−1.72**	21.53	31.50		
O(2) (CuO_2 layer, **a** axis)	−2.02	22.58	23.98		
O(3) (CuO_2 layer, **b** axis)	−2.01	22.38	22.80		
O(4) (BaO layer)	−1.93	22.26	19.73		
O(5) (antichain site)	−1.75				

TABLE II. Ionization potentials (in V) to charge-states +3 and +4, after Ref. 40, of Y and the rare-earth ions. Also presented are the radii (in Å) of the +3 charge-state ion of the element, after Ref. 31, and the weak-coupling orbital- and total-angular momentum quantum numbers L and J of the +3 rare-earth ion. Eu^{+3} has a low-lying excited state which gives it a nonzero magnetic moment despite the Hund's Rule value of $J=0$.

Element	To +3	To +4	Radius	L	J
Y	20.5	60.6	0.92	0	0
La	19.2	50.0	1.14	0	0
Ce	20.2	36.8	1.07	3	$\frac{5}{2}$
Pr	21.6	39.0	1.06	5	4
Nd	22.1	40.4	1.04	6	$\frac{9}{2}$
Pm	22.3	41.1	1.06	6	4
Sm	23.4	41.4	1.00	5	$\frac{5}{2}$
Eu	24.9	42.7	0.98	3	0
Gd	20.6	44.0	0.97	0	$\frac{7}{2}$
Tb	21.9	39.8	0.93	3	6
Dy	22.8	41.4	0.92	5	$\frac{15}{2}$
Ho	22.8	41.4	0.91	6	8
Er	22.7	42.7	0.89	6	$\frac{15}{2}$
Tm	23.7	42.7	0.87	5	6
Yb	25.1	43.6	0.86	3	3
Lu	20.9	45.3	0.85	0	0

the required generator of superconductivity, and its presence at substitutional sites[45] is signaled by the apparent failure of the compound to exhibit the charge-neutrality condition, evaluated assuming the standard values (e.g., Ba^{+2}) for the charge-states of each cation and O^{-2} for the charge-state of each oxygen.

The layers containing the hypocharged or dopant oxygen are termed the ''charge-reservoir layers.''

TABLE III. Bond-valence-sum charges (in units of $|e|$) for Nd122Nb-8, and $Nd_{1.5}Ce_{0.5}Sr_{1.7}Nd_{0.3}Cu_2GaO_9$, extracted from the data of Refs. 46 and 47, respectively.

Material	Nd122Nb-8	$Nd_{1.5}Ce_{0.5}Sr_{1.7}Nd_{0.3}Cu_2GaO_9$
Site	Charge	Charge
Nd	2.89	3.37
Ce		3.82
Ba or Sr	2.19	2.15
Nd on Sr site		2.07
Cu in cuprate-plane	1.96	2.11
Nb or Ga	4.88	2.81
O in Ba or Sr layer	−1.92	−1.80
O in Nb or Ga layer	−2.17	−2.04
O in CuO_2	−1.97	−1.96
Other O in CuO_2 layer		−2.05
O in O_2 layer		−2.30

TABLE IV. Bond-valence-sum charges (in units of $|e|$) and Madelung potentials (in V) for $EuSr_2Cu_2TaO_8$ (Eu122Ta-8), extracted from the data of Ref. 52, and computed using the self-consistent bond/charge method. Compare these charges with those in Table III for Nd122Nb-8.

Site	Charge	Potential
Eu	3.08	−32.50
Sr	1.78	−21.80
Cu in cuprate-plane	2.20	−32.70
Ta	5.02	−53.48
O in Sr layer	−1.89	18.63
O in Ta layer	−1.98	23.40
O in CuO_2 layer	−2.08	18.46

In $R122M$-8, analyses of the Ta-O and Nb-O bond-lengths indicate that both Nb and Ta are in the +5 charge-state, as expected on chemical-bonding grounds for Ta in particular. (See Tables III and IV.[46,47]) With all oxygen being O^{-2}, we find a net standard charge per cell of zero. Hence $R122M$-8 should not superconduct because it has no hypocharged oxygen—and, in fact, it does not superconduct.[48–52]

In $R222M$-10 the maximum total cation charge is $+19.5|e|$ (leaving only closed-shell ions Sr^{+2}, Cu^{+2}, Ce^{+4}, and M^{+5}), compared with $-20|e|$ for 10 fully charged oxygen ions. (See Table V for charges and Madelung potentials of Nd222Nb-10.[3] Table VI gives the trends in the charges for Pr222Nb-10, Sm222Nb-10, and Eu222Nb-10. Structural data for Gd222M-10 are not presently available.) Hence the $R222M$-10 material, like $R123$-7, is required to form substitutional hypocharged oxygen in order to balance its charge in the neutral condition, and so it should be a superconductor. It is for $R=$Nd, Sm, and Eu, but not for $R=$Pr.[1–3]

A related stoichiometric compound, $Nd_{1.5}Ce_{0.5}Sr_{1.7}Nd_{0.3}Cu_2GaO_9$, has been fabricated.[47] This material meets the charge-neutrality condition (within experimental uncertainty of its composition) with classical ionic charges if Ce is Ce^{+4} (Table III), and so has no hypocharged oxygen at substitutional ionic sites. But, in any case, the material contains approximately 0.3 Nd ions per formula unit that are magnetic and that almost certainly occupy Sr sites, where they are Cooper pair-breakers and destroy any superconductivity in Sr-O layers. The charge-reservoir oxygen model therefore predicts that the compound does not superconduct for two reasons (no hypocharged oxygen, and pair-breaking by Nd-on-Sr-site defects: Nd_{Sr})—and it does not.[47,53]

Finally Ce-doped Nd21-4 does superconduct although Nd_2CuO_4 itself is charge-balanced (Table VII), contains no hypocharged oxygen, and does not superconduct (as the charge-reservoir oxygen model would predict). The Ce-doping leads to the formation of hypocharged interstitial oxygen (as we shall see) with the interstitial sites lying at the face-centers of the Nd planes[45,54,55] and thus Ce-doping produces superconductivity.

B. Where is the primary superconductivity?

In the charge-reservoir oxygen model, the primary superconductivity is in the charge-reservoir layers, namely where the holes and hypocharged oxygen reside. The location of the holes is most easily determined from x-ray or neutron diffraction data for the bond lengths, which can then be processed using the bond-valence-sum method[39] to determine the charges on each ion and in each layer.

TABLE V. Sites in Nd222Nb-10 and the charges on those sites (in units of $|e|$), as extracted from neutron diffraction data,[3] using the bond-valence-sum method.[39] Also displayed are the corresponding Madelung potentials (in V), calculated in a point-ion model, and some ionization potentials.[40] The parentheses enclose the final charge state of the ionization. Since the $Nd^{+2} \rightarrow Nd^{+3}$ and $Nd^{+3} \rightarrow Nd^{+4}$ ionization potentials are 22.1 V and 40.4 V,[40] Nd on the Nd site is expected to be in the $+3$ charge-state. This table indicates that (i) Nd is Nd^{+3} on its normal site, but could only be the chemically unstable Nd^{+2} when isolated on a Sr site (and that no Sr-site rare-earth ion is R^{+3}, except La^{+3}); (ii) Ce is Ce^{+3} on a Nd site, but a stronger potential by 0.5 V would ionize Ce to Ce^{+4}; (iii) no other rare-earth is R^{+4} on the Nd site; (iv) Ce is Ce^{+2} on a Sr site, but a stronger potential by 0.4 V could make Ce^{+3}; (v) Cu is in the Cu^{+2} state, Sr is Sr^{+2}, and Nb is Nb^{+5}. The charge of the hypocharged oxygen is emboldened.

Site	Charge	Madelung potential	Ionization potentials		
Nd	3.31	−36.3	22.1(+3)	40.4(+4)	
Ce	3.34	−36.3	20.2(+3)	36.8(+4)	65.6(+5)
Sr	1.84	−19.8	11.0(+2)	42.9(+3)	
Cu	2.32	−31.9	20.3(+2)	36.3(+3)	
Nb	4.96	−52.3	50.6(+5)	102.1(+6)	
O(1) (NbO_2 layer)	−2.18	27.8			
O(2) (SrO layer)	**−1.72**	18.1			
O(3) (CuO_2 layer)	−1.94	18.8			
O(4) (O_2 layer)	−2.20	19.3			

In the bond-valence-sum method, which follows the empirical chemical binding ideas of Pauling,[56] the charge on the σ th ion is related both to the bond-lengths $|\mathbf{r}_{\sigma',\sigma}|$ to those neighboring ions (σ') directly bonded to it and to the site occupancies $w_{\sigma'}$, by the expression

$$|Q_\sigma| = |e| \Sigma_{\sigma'} w_{\sigma'} \exp\{[R_\sigma - |\mathbf{r}_{\sigma',\sigma}|]/\beta\},$$

where one has $\beta = 0.37$ Å, and the parameters R_σ are extracted from known bond-lengths of many chemical compounds and are tabulated in Ref. 57. Therefore, from a table of bond-lengths, it is straightforward to determine ionic charges—with a typical absolute accuracy of $\approx \pm 0.1|e|$. Results obtained for $Nd_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ are presented in Table V. To an adequate approximation, $Nd_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ contains Nd^{+3}, Ce^{+4}, Sr^{+2}, Cu^{+2}, and Nb^{+5}. All of the oxygen ions are virtually O^{-2} except those in the Sr-O layers, which are electron-deficient, being hypocharged: $O^{-1.72}$.

TABLE VI. Bond-valence-sum charges (in units of $|e|$) for R222Nb-10, for R=Pr, Sm, and Eu, from the neutron diffraction data of Ref. 3.

Material Site	Pr222Nb-10 Charge	Sm222Nb-10 Charge	Eu222Nb-10 Charge
R	3.65	3.24	3.07
Ce	3.81	3.87	3.78
Sr	1.80	1.84	1.91
Cu	2.36	2.30	2.32
Nb	4.75	5.22	5.19
O(1) (NbO_2 layer)	−2.18	−2.20	−2.21
O(2) (SrO layer)	−1.68	−1.78	−1.76
O(3) (CuO_2 layer)	−2.00	−1.97	−1.98
O(4) (O_2 layer)	−2.37	−2.24	−2.14

In the R123-7 compounds, the demonstration that there are holes in the vicinity of the Cu-O chain layers is afforded by the fact that the Cu-O chain layers and, to a lesser extent, the adjacent Ba-O layers, are positively charged (to $+0.5|e|$ and $+0.2|e|$)—when the simple valence rules would have them be neutral. (See Table I.) Hence the charge-reservoirs in R123-7 are in the vicinity of the Cu-O chains, where the hypocharged $O^{-1.72}$ is found.[37]

In R122M-8 we find that for M=Nb and R=Nd (Table III shows charges for R=Nd), the Nb ionic charge is approximately $+5|e|$, confirming our argument that led to a prediction of insulating character. Note in particular that this material has no hypocharged oxygen: all oxygen ions are essentially O^{-2}, with an approximate uncertainty of $\pm 0.1|e|$. Similar results hold for other choices of rare-earth R, such as Eu (Table IV).[52]

In R222M-10, the layers that deviate from the expectations of classical valence the most are the Sr-O layers, and are charged positive. (See Table V.) Therefore that is where the charge-reservoir is and where the holes are—on the apical oxygen atoms in these layers.[58]

In R21-4, the charge reservoir is where the hypocharged oxygen resides, namely at the interstitial site, approximately at the face-center of the Nd plane. The charges of Table VII do not reflect this fact, because the interstitial oxygen, being a defect, is not ordinarily included in the refinements of neutron diffraction data. However, the interstitial must be hypocharged, because O^{-2} has too large an ionic radius to fit at the interstitial site.[31,59,60] The radius A of O^{-Z} is approximately $A(O^{-Z}) \approx (0.375Z + 0.65)$Å, so that only oxygen considerably less-negatively charged than O^{-2} can fit at the interstitial site, which (in a hard-sphere model for $Nd_{2-z}Ce_zCuO_4$) cannot accommodate ionic oxygen with $Z > 1.23$.[60]

The interstitial dopant oxygen of Ce-doped R21-4 appears to have produced a strong Raman-scattering feature indicative of an oxygen vibration parallel to the c axis, with

TABLE VII. Sites in $Nd_{2-z}Ce_zCuO_4$ and the charges on those sites (in units of $|e|$), as extracted from neutron diffraction data,[78] using the bond-valence-sum method.[39] The cation is a virtual-crystal average of Nd and Ce. Also displayed are the corresponding Madelung potentials (in V), calculated in a point-ion model, and some ionization potentials.[40] The parentheses enclose the final charge state of the ionization. The results for $Z=0$ correspond to the ideal crystal; $Z=-1.16$ corresponds to an interstitial oxygen of charge $Z|e|$, at an apical site near the face-center of the Nd plane, but adjacent to a Ce which is displaced 0.158 Å in the **c** direction from the face-center of the rare-earth plane, away from the closest cuprate-plane, and toward the O_2 plane. This table indicates that the ions should have the following charge states on their normal sites for $Z=0$: Nd^{+3}, Ce^{+3}, and Cu^{+1} (but sufficiently close to the borderline to be Cu^{+2} in reality). For interstitial oxygen with $Z=-1.16$ we expect: Nd^{+3}, Ce^{+4}, Cu^{+1} (for the Cu ion nearest to the Ce), and Cu^{+2} for the Cu adjacent to the interstitial oxygen, which Cu experiences a Madelung potential of −32.75 V. Note that there must be an oxygen defect immediately adjacent to the Ce to ionize the Ce to Ce^{+4}. The charge of the hypocharged interstitial oxygen is emboldened.

Site	Charge $Z=0$	Charge $Z=-1.16$	Madelung potential $Z=0$	Madelung potential $Z=-1.16$	Ionization potentials	
Nd	3.09	3.10	−29.85	−35.82	22.1(+3)	40.4(+4)
Ce	3.22	4.26	−29.85	−36.90	20.3(+3)	36.8(+4)
Cu	1.83	1.83	−19.32	−17.30	20.3(+2)	36.3(+3)
O (1) (cuprate-plane)	−1.80	−1.80	23.56	24.84		
O (2) (O_2 layer)	−2.21	−2.21	24.26	23.24		
Interstitial O	0.00	**−1.16**		8.31		

the oxygen being at the apical site, a site that becomes occupied with unit probability when the crystal makes a transition from the T' crystal structure to the T structure as the rare-earth radius lengthens from that of trivalent Pr (in Pr21-4) to La (in $La_{2-\beta}Sr_\beta CuO_4$). Occupancy of this interstitial site is energetically favorable if a Ce-dopant is adjacent to it, or if the size of the rare-earth ion approaches that of La^{+3}.[61] Although there are other data suggestive of this defect,[60] and our doping picture required it,[62] we were unaware of these Raman data until they were called to our attention by Cardona[63]—and they are fully consistent with our (Ce,O) model of p-type doping by interstitial oxygen ions which form pairs with Ce.

The chemical trends in the locations of the charge-reservoirs are especially interesting, since many researchers would be astonished by our claim that the Sr-O layers are charge reservoirs. In converting R123-7 into $R122M$-8, the Cu-O charge-reservoir chains are replaced by insulating NbO_2 or TaO_2 layers, annihilating the R123-7 chain-layer charge-reservoirs and making $R122M$-8 insulating. Since BaO and SrO are electronically virtually identical (and only slightly different structurally in a first approximation[58]), the Sr-O layers and the niobate and tantalate layers are expected to be insulating in $R222M$-10, as in $R122M$-8. However, in $R222M$-10 the Sr-O bond lengths are stretched from their natural lengths, which implies that there are more holes on the oxygen of the Sr-O layer than in the Ba-O layer which has compressed bonds;[57,58,64] this facilitates the formation of hypocharged oxygen, which leads to superconductivity. Accordingly, we speculate that Sr replacement of Ba in $R122M$-8 in the formation of $R222M$-10 is partly responsible for T_c being substantial in the latter material. The next candidates for charge-reservoirs in $R222M$-10 might be the O_2 layers between the rare-earth ions, but the oxygen ions in these layers (having captured electrons from the adjacent rare-earth ions), are fully charged to O^{-2} according to the bond-valence-sum analyses of Table V, and do not form reservoirs for holes. In these compounds, interstitial oxygen appears to be ruled out as a p-type dopant, because of steric constraints.[51] The partitioning of high-temperature superconductors into charge-reservoirs and cuprate-planes (the charge-transfer hypothesis[44,65,66]) implies that the charge-reservoirs are separate from the cuprate-planes, eliminating the cuprate-planes and leaving only the Sr-O layers as possible charge-reservoirs in $R222M$-10. The charge reservoirs are those layers that contain the hypocharged oxygen ions: precisely those layers that show up in the bond-valence-sum analyses as containing extra holes. Therefore the charge-reservoir layers in Nd222Nb-10 and its sister compounds are the Sr-O layers.

The fact that the charge-reservoirs move from the Cu-O chain layers in R123-7 to the Sr-O layers in $R222M$-10, to the interstitial regions of Nd21-4, and are insulating in $R122M$-8, suggests that in this model the superconductivity must change its location in the crystal structure. Only hypocharged oxygen in the charge-reservoirs can supply the holes necessary for p-type superconductivity, and if the charge-reservoirs move, the locus of superconductivity must move too. Further evidence for different superconducting regions in these different materials includes the fact that the necessary Ce content for maximum T_c changes from zero in Nd123-7 to $z\approx0.15$ in $Nd_{2-z}Ce_zCuO_4$ to $z\approx0.5$ in Nd222Nb-10, and the effect on superconductivity of Pr-doping changes from *poisonous* in Pr123-7[23] (or, more precisely, in $PrBa_{2-u}Pr_uCu_3O_7$[15–22]) and in Pr222Nb-10 to *advantageous* in $Pr_{2-z}Ce_zCuO_4$.[2,67,68] Other assignments of the charge-reservoirs lead to logical inconsistencies. For example, since the Cu-O chains are in the charge-reservoirs in R123-7, the natural expectation would be that the MO_2 layers are the charge-reservoirs in $R122M$-8. Yet this assignment would leave unanswered why $R122M$-8 does not superconduct, while R123-7 and $R222M$-10 do. It also is inconsistent with the bond-valence-sum charges (Tables I, III, IV, V, VI, and VII), which place the holes in different layers in the superconductors and reveal no hypocharged oxygen in $R122M$-8. These data all seem to indicate that both the charge-reservoirs and the primary superconducting regions are different in the different materials.

C. Successful prediction of T_c

In the charge-reservoir oxygen model, a prescription for predicting T_c is to use the result

$$T_c \approx (15\ \text{K/Å})d,$$

where d is the distance between a charge-reservoir oxygen ion and the nearest cuprate-plane Cu ion.[69] Since this empirical rule was based in part on data for $YBa_2Cu_3O_7$ homologues and for $Nd_{2-z}Ce_zCuO_4$, it is guaranteed to describe the critical temperature for $R123$-7 and $R21$-4 homologues rather well.

In the case of the $R123$-7 homologues, the charge-reservoir oxygen model predicts that all of the homologues will have essentially the same superconducting critical temperature T_c, which for these materials is ≈ 90 K. Until recently, it was widely assumed that Pr123-7 was an exception to the $T_c \approx 90$ K rule for all $R123$-7 compounds, but as a result of a prediction that magnetic Pr on Ba sites breaks Cooper pairs and destroys superconductivity,[23] a number of experiments first detected granular superconductivity,[15–17] followed by experiments reporting superconductivity in single-crystals and in bulk Pr123-7 samples[18–22] that were grown using conditions known to minimize Pr-on-Ba-site (Pr_{Ba}) defects. The other $R123$-7 compounds that do not superconduct all involve large ions R^{+3}: Ce^{+3} in $Y_yCe_{1-y}123$-7 or $Nd_yCe_{1-y}123$-7, and Cm^{+3} in Cm123-7, and so it is reasonable, following the data for Nd in $NdBa_{2-u}Nd_uCu_3O_7$[70] and for Pr in $PrBa_{2-u}Pr_uCu_3O_7$,[71] to conclude that the largest ions are highly soluble on Ba sites, where they destroy Cooper pairs and superconductivity, if the impurities are magnetic. (Modest amounts of large-radius non-magnetic La^{+3} ions on Ba sites are known to *not* destroy superconductivity in $YBa_{2-v}La_vCu_3O_7$[72] and $Y_{1-\lambda}Ca_\lambda Ba_{2-\lambda}La_\lambda Cu_3O_7$,[73] demonstrating that the destruction of superconductivity is due to the *magnetic* moments, not the size, of the large ions—which happen to be highly soluble on Ba sites by virtue of their large size.)

In the case of $R222M$-10, where the charge-reservoirs are the Sr-O layers and so we have $d \approx 2.0$ Å,[74] the value of the critical temperature T_c has been predicted to be $T_c \approx (15\ \text{K/Å})d \approx 30$ K—essentially equal to the observed value $T_c \approx 28$ K,[3–9] which is the same for $M=\text{Ta}$ and $M=\text{Nb}$. This fact also hints that the MO_2 layers are not the loci of the primary superconductivity, which might be expected to sense a difference between Ta and Nb if those layers were strongly superconducting.

Thus, by following the established procedures of the oxygen model, we obtained a successful prediction of the critical temperatures T_c for $R222$Nb-10 and $R222$Ta-10. The model also succeeded in predicting that T_c for properly prepared Pr123-7 must be ≈ 90 K, at a time when Pr123-7 had not been properly prepared and had not superconducted at all. To our knowledge, there have been only two superconductors for which T_c has been *predicted* successfully: (i) $SrTiO_3$ with $T_c = 1$ K, predicted by Cohen,[75] and (ii) $PrBa_2Cu_3O_7$ with $T_c \approx 90$ K, predicted by us,[23] and recently shown to superconduct at approximately that temperature.[15–22] Moreover, with the identification of the charge-reservoirs in the $R222M$-10 compounds as the Sr-O layers, the empirical rule prescribes and ‘‘post-dicts’’ the critical temperatures of $R222$Nb-10 and $R222$Ta-10 to be $T_c \approx 30$ K, in agreement with the $T_c \approx 28$ K observations.[2,3]

D. Why Nd222M-10 is different from $Nd_{2-z}Ce_zCuO_4$

The astute reader will recognize that the crystal structure of Nd222M-10, [Fig. 1(c)] is almost identical to that of $Nd_{2-z}Ce_zCuO_4$ [Fig. 1(d)], except that $Nd_{2-z}Ce_zSr_2Cu_2NbO_{10}$ has (i) two additional Sr-O planes, (ii) one additional NbO_2 plane, and (iii) one additional CuO_2 cuprate plane. That is, $Nd_{1-z}Ce_zSr_2Cu_2NbO_{10}$ is $Nd_{2-z}Ce_zCuO_4$ sandwiched between these extra planes. One might speculate that the extra planes are insulating, and that the material is actually a superconducting superlattice containing slabs of ‘‘superlattice’’ $Nd_{2-z}Ce_zCuO_4$ layered with additional $SrO/NbO_2/SrO/CuO_2$ layers. As a result, except for a few superlattice and confinement effects, the ‘‘superlattice’’ $Nd_{2-z}Ce_zCuO_4$ superconductor would be a slightly perturbed version of ‘‘free’’ $Nd_{2-z}Ce_zCuO_4$. Since the critical temperature for ‘‘free’’ $Nd_{2-z}Ce_zCuO_4$ is $T_c \approx 24$ K,[28] close to the 28 K for Nd222Nb-10, this argument appears on the surface to be rather appealing.

However, several facts indicate that this cannot be the case: (i) The optimal Ce content in ‘‘free’’ $Nd_{2-z}Ce_zCuO_4$ is $z \approx 0.15$, whereas in $Nd_{2-z}Ce_zSr_2Cu_2NbO_{10}$ the corresponding Ce concentration for ‘‘superlattice’’ $Nd_{2-z}Ce_zCuO_4$ is $z \approx 0.5$; and ‘‘free’’ $Nd_{1.5}Ce_{0.5}CuO_4$ neither exists nor would superconduct if it did,[76] since the maximum Ce solubility is $z \sim 0.2$.[77] These differences indicate that the detailed role of Ce in the two superconductors is somehow not quite the same. Indeed it proves that Ce does not simply act as a dopant, but has a more complex role in the superconductivity of these materials. (ii) A comparison of the charge distributions shows that $Nd_{2-z}Ce_zCuO_4$ (Table VII[78]) and Nd222Nb-10 (Table V) are indeed different. (Note, for example, the hypocharged oxygen $O^{-1.72}$ in the Sr-O layer, and the charges on the Cu sites.) At the same time, in a standard classical point-charge analysis, the Sr-O plane has a net charge of zero, the NbO_2 layer has a charge of $|e|$, and the CuO_2 layer is charged $-2|e|$, giving a net of $-|e|$ for the additional layers $SrO/NbO_2/SrO/CuO_2$ and hence a compensating charge of $+|e|$ for the ‘‘superlattice’’ $Nd_{2-z}Ce_zCuO_4$ layers in the Nd222Nb-10 superlattice. Either this net charge is fictitious and the additional layers are actually uncharged, or not. If it is fictitious, then the additional layers must contain some hypocharged oxygen to achieve the uncharged state—and so the charge-reservoir is in a different location in the superlattice from in ‘‘free’’ $Nd_{2-z}Ce_zCuO_4$. If the charge is real, then the additional planes have a net charge in Nd222Nb-10 and ‘‘superlattice’’ $Nd_{2-z}Ce_zCuO_4$ in the superlattice must carry a compensating charge, rather than be neutral as in ‘‘free’’ $Nd_{2-z}Ce_zCuO_4$. It is difficult to see how charged additional layers might be insulating. And in any case, ‘‘superlattice’’ $Nd_{2-z}Ce_zCuO_4$ in this Nd222Nb-10 superlattice must be different from ‘‘free’’ $Nd_{2-z}Ce_zCuO_4$. (iii) A bond-valence-sum analysis of $Nd_{2-z}Ce_zCuO_4$ puts the

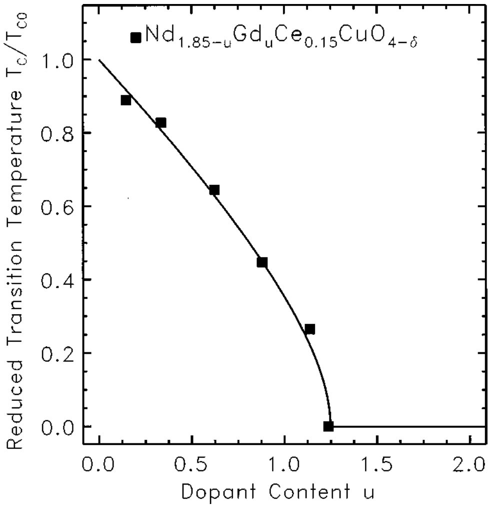

FIG. 2. Critical temperature T_c of $Nd_{1.85-u}Gd_uCe_{0.15}CuO_4$, after Ref. 29, vs Gd dopant content u, demonstrating that $L=0$ Gd^{+3} destroys the superconductivity of $Nd_{2-z}Ce_zCuO_4$. The solid line is the pair-breaking theory of Abrikosov and Gor'kov.[80] The explanations of this degradation of T_c that have been proposed are (i) pair breaking by Gd^{+3} that is not forbidden by crystal-field splitting and (ii) a mechanical effect similar to that caused by Y doping.[30] Only the former provides a fully consistent explanation of the data.[50]

holes in the $Nd_{2-z}Ce_zO_2$ layers, different from the case for $Nd_{2-z}Ce_zSr_2Cu_2NbO_{10}$, where the holes are in the charge-reservoir Sr-O layers. The charge $-1.72|e|$, which is the same for hypocharged oxygen in the Cu-O chains of Nd123-7 and in the Sr-O layers of Nd222Nb-10, is the signal that the Sr-O layers are the charge-reservoirs. We conclude that the charge-reservoirs are in different locations in the two materials. (iv) Replacement of all the Nd in $Nd_{2-z}Ce_zCuO_4$ by Gd destroys the superconductivity[29,79] (Fig. 2[29,80,81]), while a corresponding replacement in $Nd_{2-z}Ce_zSr_2Cu_2NbO_{10}$ does not.[10,11] Because $R222M$-10 superconducts for the rare-earth $R=Gd$ (with orbital angular momentum quantum number $L=0$, despite having total angular momentum $J=7/2$), we deduce that crystal-field splitting plays no role in the superconductivity of Nd222Nb-10. Hence the insensitivity of the $R222M$-10 superconductivity to the pair-breaking rare-earth's magnetic moment, even for $R=Gd$, must be attributed to the fact that the exchange-scattering range of the magnetic rare-earth does not extend to the superconducting condensate. This implies that the condensate is most likely in the Sr-O layer.[82]

The situation in the $R21$-4 compounds is somewhat more complex. The proximity of the magnetic rare-earth ions R to the superconducting condensate is virtually guaranteed in this system, because the rare-earth is directly bonded to every other ion except Cu. Again, the first question to be asked is why these magnetic rare-earth ions, including Pr^{+3},[24] but excepting $L=0$ Gd^{+3} which destroys superconductivity (Fig. 2), do not disrupt the superconductivity when they appear to be adjacent to whatever condensate might be present. Here, crystal-field-splitting affords perhaps the only potential answer and indicates that the superconducting condensate is near the rare-earth site, within the range of the exchange-scattering: Crystal-field splitting can render the pair-breaking capabilities of a rare-earth magnetic moment impotent,[83] provided the magnetic impurity does not have zero orbital angular momentum $L=0$, as do Gd^{+3} and Cm^{+3}, in which case there is no crystal-field splitting. With pair-breaking operative for the $L=0$ ions, Gd21-4 and $Cm_{2-z}Th_zCuO_4$ should not superconduct—and do not.[84–86] Indeed, Soderholm *et al.* present evidence that the failure of $Cm_{2-z}Th_zCuO_4$ to superconduct is a magnetic effect,[85,86] consistent with our proposal here.

However, while crystal-field splitting is necessary to explain why $R21$-4 with magnetic rare-earth ions R can superconduct at all, it is clearly not the only effect on $R21$-4 superconductivity; there is clearly a size-effect also. Indeed, we shall argue that there are *two* size effects, one related to oxygen *doping* and the other associated with the ability of the rare-earth ions to *form* stable bonds.

Perhaps the best evidence of a size effect comes from $(Y_yR_{1-y})_{2-z}Ce_zCuO_4$ alloys, which cannot be fabricated for $y\rightarrow 1$,[87] but Y (which is nonmagnetic, with $J=0$, has $L=0$, and so does not break Cooper pairs by spin-flip scattering) nevertheless exhibits a more rapid suppression of T_c with y than $J\neq 0$ magnetic Gd in $(Gd_yR_{1-y})_{2-z}Ce_zCuO_4$ does.[30] This more-rapid suppression is clearly not a crystal-field effect, but a size effect.[30,60,88] However, based on recent work,[60,62,89] we conclude that there are *two* size effects in the $R21$-4 compounds: (i) Ce doping appears to actually be p-type doping by (Ce, interstitial-oxygen) pairs, and each cage surrounding an interstitial oxygen ion near the face-center of an R plane consists of eight oxygen ions from the O_2 and CuO_2 layers; this cage becomes too small as the rare-earth size decreases from Pr^{+3} to smaller than Gd^{+3} or Tb^{+3}. For smaller R^{+3}'s the cage no longer provides enough space for the p-type doping required for superconductivity (because the cage must hold O^{-Z} with $Z>1$ if the interstitial has both captured a Ce electron and donated $Z-1$ holes to the valence band). When this happens, one can no longer *dope* R_2CuO_4 p-type with Ce.[60,62] (ii) Simultaneously the cage surrounding the rare-earth ion (which in the simplest models is the same size as the interstitial oxygen cage), becomes too large for the rare-earth to bond to its neighboring oxygen ions, because the rare-earth size decreases faster than the cage size, until the rare-earth's bonds to the neighboring oxygen ions are stretched by more than several percent ($<10\%$[90]) and break. When this condition is met, one can no longer *fabricate* R_2CuO_4 without high pressure.[89] $(Y_yR_{1-y})_{2-z}Ce_zCuO_4$ is an example of the second size effect. Since crystal-field splitting must affect the superconductivity in $Nd_{2-z}Ce_zCuO_4$ for it to superconduct, and clearly does not have a role in the superconductivity of Nd222Nb-10 (which we know, because its homologue Gd222Nb-10 superconducts), the superconducting condensates in the two materials are necessarily different in an important geometrical way: the data indicate that Gd on a Nd site in $Nd_{2-z}Ce_zCuO_4$ is very likely a nearest-neighbor to the superconducting condensate and breaks Cooper pairs, while Gd in $Gd_{2-z}Ce_zSr_2Cu_2NbO_{10}$ definitely is remote from the superconducting condensate, which must lie beyond the range of exchange scattering by Gd.

Recall that the charge-reservoir model places the primary superconductivity in the region of dopant oxygen, namely (i) at interstitial oxygen occupying a face-centered site in the Nd plane and directly bonded to the adjacent Cu in

$Nd_{2-z}Ce_zCuO_4$, but (ii) at the very different oxygen sites in the Sr-O layers of $Nd_{2-z}Ce_zSr_2Cu_2NbO_{10}$. As a result, in the charge-reservoir model (and in the data) crystal-field splitting affects the superconductivity in $Nd_{2-z}Ce_zCuO_4$, but not in $Nd_{2-z}Ce_zSr_2Cu_2NbO_{10}$. A trivial consequence of this picture is that $Gd_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ must superconduct, as it does.[3]

III. CUPRATE-PLANE MODELS

Most current models of high-temperature superconductivity are based on superconducting cuprate-planes doped by carriers (normally holes) which are transferred to those planes from the charge-reservoir layers. Without regard for the short-comings of either the cuprate-plane picture of superconductivity or the hypothesis of charge-transfer from the charge-reservoirs to the cuprate-planes,[23,34,59,66,69,91–93] we shall discuss its predictions for the behavior of R123-7, R122M-8, R222M-10, and R21-4.

A. *R*123-7

Three major experimental facts in R123-7 compounds are (i) $PrBa_{2-u}Pr_uCu_3O_7$ does not superconduct,[94] while most other R123-7 compounds do,[23] (ii) $GdBa_2Cu_3O_7$ superconducts but isoelectronic $CmBa_2Cu_3O_7$ does not,[95,96] and (iii) Nd on the rare-earth site of $NdBa_2Cu_3O_7$ has no adverse effect on T_c, but Nd on the Ba site of $NdBa_{2-u}Nd_uCu_3O_7$ destroys superconductivity,[38] while the same appears to be untrue for La on the Ba site in $YBa_2Cu_3O_7$.[72,73] (Sm, Eu, and Gd exhibit similar behavior to Nd.[97])

(i) Attempts to explain the nonsuperconductivity of Pr123-7 based on models with all of the Pr on rare-earth sites and invoking hybridization have been contradicted by the experimental fact that using pressure to increase the hybridization in Nd123-7, a R123-7 homologue, until the hybridization reached the Pr123-7 level, not only failed to destroy the superconductivity (as expected for cuprate-plane superconductivity), but enhanced it.[98] (The charge-reservoir oxygen model ascribes the nonsuperconductivity of Pr123-7 to pair-breaking by Pr ions on Ba sites,[23] not to hybridization.)

These pressure experiments can be reconciled with cuprate-plane superconductivity and hybridization only if the application of pressure eliminates the *secondary or induced* superconductivity[99] in the cuprate-planes of R123-7 compounds, while enhancing the *primary* superconductivity in the Cu-O chains or charge-reservoirs. However, if this were true, superconductivity in Pr123-7[15–22] would reside exclusively in the reservoirs, in agreement with the fundamental premise of the charge-reservoir oxygen model, which locates the primary superconductivity there.

(ii) No explanation of the differences between superconducting Gd123-7 and non-superconducting isoelectronic Cm123-7 has been offered within the context of cuprate-plane models of superconductivity. Except for a slight difference in the radii of Gd^{+3} and Cm^{+3}, and the fact that the Cm $5f$ electrons play the role of the Gd $4f$ electrons, these two compounds are virtually identical. (The charge-reservoir oxygen model ascribes the difference to pair-breaking by larger-radius Cm ions which are more soluble on Ba sites, where they break Cooper pairs.)

(iii) Although a cuprate-plane-model explanation of the destruction of superconductivity by Ba-site Nd has been given in terms of hole-filling,[100] hole-filling would occur only if the Ba-site Madelung potential were sufficient to ionize the rare-earth on that site to R^{+3} without additional oxygen being present—which is never the case. Moreover, no explanation of the absence of comparable effects by trivalent La[72] has been presented. (The charge-reservoir oxygen model attributes this difference to the nonmagnetic character of La^{+3} in contrast to magnetic pair-breaking by Nd^{+3} or Pr^{+3} on Ba sites.)

Clearly explanations of these and other major facts, in terms of a cuprate-plane model, are needed before that model can be accepted.

B. *R*122*M*-8

The initial attempts to grow R122M-8 were probably intended to alter the doping of the cuprate-planes of R123-7 by replacing the Cu ions of the Cu-O chain layers with Nb. (They obtained NbO_2 layers.) The expectation, based on a cuprate-plane picture of superconductivity, was that R122M-8 would superconduct, but it did not (for either $M=$Nb or $M=$Ta).[6,101,102]

It appears to us that the reason the R122Nb-8 compounds were expected to superconduct with higher critical temperatures than R123-7 was that Nb was perhaps expected to display a charge-state of $+3$, rather than $+5$. Our analyses of the bond-lengths in these compounds in terms of bond-valence-sum charges, indicate that the Nb charge-state is invariably $+5$. So perhaps the failure of the cuprate-plane model to predict the insulating character of the R122M-8 compounds was simply due to a valence that was incorrectly estimated—and the material, with a $+5$ charge-state, might possibly have been expected to be an insulator even in the cuprate-plane framework. Nevertheless the cuprate-plane model has not seemed capable of predicting which compounds will superconduct and which will not.

C. *R*222*M*-10

When R122M-8 compounds turned out to be insulators, the efforts to synthesize R222M-10 were obviously based on the notion that R222M-10 might superconduct—although we are unaware of any suggestion based on cuprate-plane theories to that effect. Nevertheless, looking at the R222M-10 crystal structures, which are identical to those of R123-7 in the cuprate-planes and adjacent planes, one might easily suggest that R222M-10 would have the same (local) density of states as R123-7, and therefore should superconduct at about $\approx$90 K (the same critical temperature as R123-7), if the additional rare-earth ion and O_2 layer were to provide the necessary holes.

This suggestion is inconsistent with the facts in two ways: (i) the bond-valence-sum analysis indicates that the oxygen ions in the new layer between the two rare-earth ions are all essentially charged to O^{-2}—and so do not reflect the anticipated high density of holes in that region, and (ii) the observed value of T_c is much lower than the expected 90 K, $T_c\approx 28$ K. Therefore the cuprate-plane picture seems to predict that R222M-10 compounds should superconduct, but with $T_c \approx 90$ K. Thus this explanation based on cuprate-plane superconductivity does not seem to be valid.

A different viewpoint that might result from the cuprate-plane picture of superconductivity is that Nd222Nb-10 is merely a superlattice of repeated slabs of ''superlattice'' $Nd_{2-z}Ce_zCuO_4$ and $SrO/NbO_2/SrO/CuO_2$, so that the material should have nearly the superconducting properties of hypothetical $Nd_{2-z}Ce_zCuO_4$. But $Nd_{2-z}Ce_zCuO_4$ has not been fabricated with Ce content z in excess of $z \sim 0.2$, the solubility limit, and hence does not superconduct.[2,77,103] In any case, explanations are needed of why Gd21-4 does not superconduct while Gd222M-10 does, and why Pr222M-10 does not superconduct while Pr21-4 does. After all, if both Nd21-4 and Nd222Nb-10 contain the same basic superconducting entity, changing the Nd in both materials to Gd (or Pr) should produce new materials with the same superconducting behavior—but does not: one material superconducts; the other does not. These facts remain unexplained by cuprate-plane models.

A major question unanswered by cuprate-plane models of superconductivity is: Why do not all compounds with cuprate-planes have nearly equal critical temperatures T_c for optimal doping, especially if the superconductivity is supposedly two-dimensional? After all, the superconducting entity is ideally the cuprate-plane. Of course, from a practical viewpoint, the superconducting entity is purportedly the cuprate-plane and all atoms within a coherence length. But even this definition has the observed critical temperatures in dramatic conflict with data.[69]

D. *R*21-4

In a cuprate-plane picture of superconductivity, Nd21-4 and its T'-structure R21-4 superconducting homologues are n-type, with their charge-reservoirs having been doped by the electron liberated during the $Ce^{+3} \rightarrow Ce^{+4}$ transition. However, our Madelung potential calculations for $Nd_{1.85}Ce_{0.15}CuO_4$ yield a potential at the Nd site of -30 V[78] (Table VII), too small in magnitude to ionize Ce to the Ce^{+4} charge-state, which requires -37 V.[40] (See Table VII.) We conclude that Ce in *ideal* $Nd_{2-z}Ce_zCuO_4$ on a Nd site is necessarily Ce^{+3}. However, Ce^{+3} is so large (1.07 Å compared with Nd^{+3}'s 1.04 Å or Eu's 0.98 Å) that its size may preclude it from having significant solubility in Nd_2CuO_4 and very likely will severely limit its solubility in Eu_2CuO_4.

Measurements suggest that the actual charge state of Ce in $Nd_{2-z}Ce_zCuO_4$ is Ce^{+4}: Tranquada *et al.*[104] and Liang *et al.*,[105] have presented evidence to support their position that Ce is tetravalent Ce^{+4}: (i) the addition of one Ce to Nd_2CuO_4 changes roughly one Cu^{+2} into a Cu^{+1}; (ii) Ce in Nd_2CuO_4 has approximately a charge of $+3.5|e|$, by comparison with CeO_2, which exhibits a similar Ce L_3 near-edge structure and similar bond-valence-sum charges.[106] (iii) Seaman *et al.*[107] studied Eu_2CuO_4 doped with Ce, and were unable to detect the magnetic signature expected of Ce^{+3}. Thus the data appear to indicate that Ce is Ce^{+4}, while the theory of electrostatics claims Ce^{+3} for $Nd_{2-z}Ce_zCuO_4$ with an *ideal* crystal structure.

Our own interpretation of these experimental facts is that the local environment of Ce must include an adjacent interstitial oxygen ion for it to assume the Ce^{+4} charge-state and that the observation of Ce^{+4} in $Nd_{2-z}Ce_zCuO_4$ implies the existence of interstitial oxygen adjacent to the Ce. Extended x-ray absorption fine-structure data[108] support this viewpoint: they show that Ce in Nd21-4 bonds to an oxygen, and moves away from the cuprate-plane in the **c** direction by a distance of order ~0.1 to 0.2 Å. By introducing an apical oxygen at the face center of the Nd plane, and moving it a distance 0.158 Å toward the O_2 layer, we were able to obtain a situation in which the Madelung potential at a rare-earth or Ce site exceeded the ionization potential of Ce to Ce^{+4}. (See Table VII.) In this case the bond-valence-sum charge on the interstitial oxygen became $-1.16|e|$, clearly hypocharged. Thus the effect of Ce in Nd_2CuO_4 is not direct doping of the Cu in the cuprate-planes with *delocalized* electrons (as assumed); instead each Ce bonds with an oxygen-interstitial at the apical site, and the initially neutral interstitial-oxygen ionizes by capturing a Ce electron, leaving the interstitial oxygen with a still unfilled $2p$ shell. Thus Ce-doping produces p-type (hole) carriers, with the holes coming from the interstitial oxygen.

The *local* charge redistributes in response to the (Ce, interstitial-O) defect pair, and, as a result, the Cu ion that is closest to the Ce assumes the Cu^{+1} charge state (as observed[104]), while more distant Cu ions retain the Cu^{+2} charge-state. (See Table VII.)

This picture is consistent with the +4 nominal valence of Ce in molecular CeO_2, which has an effective charge determined from x-ray spectra of $+3.5|e|$. CeO_2's bond-valence-sum charge is $4.38|e|$.[106] (The oxygen charge is $-2.19|e|$.) With these revised charges, we have computed (again, in a point-ion model) the Madelung potentials of the molecule, finding -45.6 V and $+4.2$ V at the Ce and O sites. Note that the Ce-site Madelung potential, being greater than 36.8 V in magnitude, is adequate to ionize Ce^{+3} to Ce^{+4} in the molecule CeO_2. Thus the (Ce, interstitial-O) doping picture and the CeO_2 molecular data are consistent with one another.

Using only simple ideas, we conclude on the basis of electrostatics that isolated Ce in *ideal* $Nd_{2-z}Ce_zCuO_4$ must actually be in the Ce^{+3} charge-state, but that Ce in a *real* material will invariably bind to nearby oxygen, and form Ce^{+4} plus an interstitial hypocharged oxygen which generates p-type superconductivity. In addition to the electrostatics arguments, Ce^{+3} must satisfy steric constraints: its radius is larger than Nd^{+3}'s and much larger than Eu^{+3}'s and so (unlike Ce^{+4}) there is some question concerning whether the Ce^{+3} will dissolve adequately and fit on its proposed site. When one adds to these facts the evidence that the superconductivity in $Nd_{2-z}Ce_zCuO_4$ is indeed p-type,[54,55,109–111] the cuprate-plane model's explanation of superconductivity in Nd21-4 and its homologues appears inadequate.

IV. PREDICTIONS FOR Nd222*M*-10

The test of any model lies in its genuine *predictions of the outcome of future experiments*; it is much more difficult to predict the outcome of a future experiment than to reconcile that experiment, after the fact, with a particular model. Fortunately, the R222M-10 compounds are not thoroughly studied, and so there are a number of simple experiments that can be conducted on them whose outcomes can be predicted on the basis of either the charge-reservoir oxygen model or cuprate-plane models of superconductivity. The outcome of these experiments should help determine which theory (if either) is valid.

A. Doping character

In the charge-reservoir oxygen model, $R222M$-10 has p-type doping character. In the charge-reservoir model of $Nd_{2-z}Ce_zCuO_4$, which is very specific, the Ce replaces a Nd and bonds to adjacent interstitial oxygen.[54] The superconductivity is then generated by an interstitial apical oxygen ion. Hence we speculate that a role of the Ce is to stabilize the lattice, to form (Ce, interstitial O) defects, and to displace oxygen to an adjacent interstitial site where the oxygen is hypocharged and the Ce ionizes to Ce^{+4}.[28,112] Probably similar physics holds to some slight extent for Nd222M-10, although the Ce doping, in a classical approximation, is still insufficient to make Nd222M-10 n-type, because it leaves a net charge per formula unit of $-0.5|e|$. Furthermore, our analyses of the differences between $Nd_{2-z}Ce_zCuO_4$ and Nd222M-10 lead us to conclude that the interstitial oxygen does not form as easily in $R222M$-10:[113] the primary hypocharged oxygen is in the Sr-O layers of $R222M$-10.

In cuprate-plane models, the issue of p-type versus n-type superconductivity is not completely clear. The presence of Ce in the average cation $Nd_{0.75}Ce_{0.25}$ of Nd222M-10 suggests that the Nd222M-10 may be n-type, as many workers assume that $Nd_{2-z}Ce_zCuO_4$ is, despite recent evidence that $Nd_{2-z}Ce_zCuO_4$ is indeed p-type.[54,109–111] However, charge-balancing arguments suggest that $R222M$-10 is p-type, because some of its oxygen needs to be hypocharged and hence capable of donating holes to compensate for a nominal classical charge of $-0.5|e|$ per formula unit.

Thus we have the charge-reservoir-oxygen model's clear prediction that $R222M$-10 and $R21$-4 are both p-type, in contrast with the cuprate-plane-model's possible predictions that either both are n-type, or $R21$-4 is n-type and $R222M$-10 is p-type.

B. Pair breaking

In the charge-reservoir oxygen model, of the cation sites in Nd222M-10, only the cuprate-plane Cu sites, the Sr-O layer Sr sites, and the M sites of the niobate or tantalate layers are near-neighbors to the Sr-O layer oxygen ions on which the Cooper-pair holes must reside. Since the exchange interaction is short-ranged, only magnetic impurities on those sites are expected to exchange-scatter holes initially bound into Cooper pairs, flipping spins and suppressing T_c. Rare-earth-site impurities, in particular, should not exchange-pair-break in the superconducting condensate, because they are out of range.

Magnetic impurities on cuprate-plane Cu sites have been extensively studied in other materials, and so we predict their behavior in $R222M$-10, based on that experience.[91] Ni or Zn should have predictable effects on T_c: (i) of order ~1% Ni should depress T_c to zero (as in $Nd_{2-z}Ce_zCuO_4$), and (ii) about six times as much Zn should be required to destroy superconductivity. If this result is obtained, it will be consistent with the Bardeen-Cooper-Schrieffer or BCS[114] theory of superconductivity: the extra scattering associated with the (magnetic) exchange of Ni breaks Cooper pairs in addition to any pair-breaking by the nonmagnetic long-ranged potential, which is about the same for Ni and Zn, and chemical in origin. Furthermore, in the charge-reservoir model, the impurity site, namely a cuprate-plane Cu site, is adjacent to (and bonded to) an oxygen in the charge-reservoir, and so the Cooper pairs (whose holes reside on charge-reservoir oxygen ions) definitely lie within the range of the exchange scattering.

To make the corresponding prediction for a cuprate-plane model of Nd222M-10, we note that the cuprate-plane and its two adjacent layers, R and Sr-O are essentially the same as observed in $R123$-7. The main difference is that Ba of $R123$-7 has been replaced by isoelectronic Sr in $R222M$-10.[58] Therefore, both Zn and Ni should behave as in $R123$-7: as very weak pair-breakers, with the critical dopant content u_c required to drive T_c to zero being about 0.165 for Zn and about 0.425 for Ni.[91] This reversal of roles of (magnetic) Ni and (nonmagnetic) Zn from the normal expectation of Abrikosov-Gor'kov pair-breaking theory[80,81] is believed (by advocates of superconductivity that is primarily in the cuprate-planes) to be a consequence of spin-fluctuation pairing of carriers—although it is probably due in reality to the formation of microphases and the different solubilities of Ni and Zn on the two inequivalent Cu sites;[115,116] there are very strong arguments to exclude spin-fluctuation pairing as a general mechanism of high-temperature superconductivity.[91,93]

C. Role of Pr

Why is it that Pr222M-10 does not superconduct when its homologues do?[7] Hole filling by Pr^{+4}'s electrons has been ruled out experimentally.[117] Similar behavior occurs for Pr in $R123$-7 compounds, where Pr substitution for Y in $YBa_2Cu_3O_7$ causes T_c to drop to zero unless special care is used in preparing the material—care to keep Pr ions off Ba sites. In contrast, Pr21-4 superconducts.[24] The trends in the Meissner fractions for $R222M$-10, show that these fractions are qualitatively consistent with the large-radius Sr-site trivalent rare-earths participating in pair-breaking.[118,119] The explanation[23] of the failure of Pr123-7 to superconduct[120] (until recently[15–22]), now confirmed by several experiments, is that Pr occupies Ba sites in addition to Pr sites in Pr123-7, where it causes suppression of the critical temperature, presumably by breaking Cooper pairs in the adjacent charge-reservoir. In $Y_{1-y}Pr_yBa_2Cu_3O_7$, isolated Ba-site Pr, because of the size of the Madelung potential, can only adopt a chemically unstable Pr^{+2} charge-state in the *ideal* crystal structure. But when accompanied by oxygen on an adjacent antichain site in a Cu-O chain layer, the magnitude of its Madelung potential exceeds the 21.6 V needed to produce Pr^{+3}. (See Table I) In either case Pr has a nonzero magnetic moment that breaks Cooper pairs in adjacent layers. The Pr doping of $R123$-7 compounds destroys the superconductivity by pair breaking due to Pr's magnetic moment. Note that Pr on the Ba site, plus antichain oxygen, *locally* converts a Cu-O chain into another cuprate-plane, but simultaneously *decreases* both T_c and the Meissner fraction—evidence *against* cuprate planes as the primary loci of superconductivity.

Similarly, in Pr222M-10 we propose that Pr occupies Sr sites naturally.[117] Therefore Pr on a rare-earth site, in particular, will not break Cooper pairs because it is too distant from the superconducting condensate in the charge reservoir; but Pr on a Sr site will. Such occupation of Sr sites by Nd (which is not very different from Pr) has been reported in some of these niobate and tantalate compounds,[47] and at Sr sites the magnetic moment of any rare-earth ion necessarily breaks Cooper pairs in the charge-reservoir Sr-O layers. The pair-breaking by Pr on the Sr sites of Pr222Nb-10 is so similar to the effect of Ba-site Pr in Pr123-7 that it must be the explanation of why Pr222Nb-10 does not superconduct.

We expect the larger-radius rare-earth ions, which have the smallest size mismatches with Sr^{+2}, to occupy the Sr sites in R222Nb-10 with higher solubilities than the smaller radius rare-earths. Trivalent La, Ce, Pr, and Nd should be most soluble on Sr sites, with the heaviest rare-earths being insoluble on Sr sites. When on a Sr site of *ideal* Pr222Nb-10, Pr is expected to express the chemically unstable charge-state Pr^{+2} and produce no long-ranged scattering of carriers, because a Madelung potential of roughly -20 V at the Sr site (Table V) will ionize only La of the rare-earths to the R^{+3} charge-state; all of the other rare-earths will ordinarily be the less-stable R^{+2} in ideal R222Nb-10.

There are several important differences between the situations with Pr123-7 and Pr222Nb-10: (i) In Pr222Nb-10 there are no vacant sites nearby, analogous to the antichain sites of Pr123-7, for extra oxygen ions, and hence it is more difficult for oxygen to ionize the Pr to Pr^{+3} and to accept the extra electron associated with hypothetical Pr^{+3} replacement of Sr^{+2}. This raises concerns about (local) charge-neutrality. (ii) Pr on a Sr site on Pr222Nb-10 has a Madelung potential of -19.54 V, too weak in comparison with the 21.62 V ionization potential[40] for causing Pr^{+2} to become Pr^{+3}. (iii) Since Sr^{+2} has a radius that is only ≈ 0.08 Å larger than that of Nd^{+3}, we expect that the rare-earths will be somewhat better size-matched and hence more soluble on Sr sites in R222Nb-10 than on Ba-sites in R123-7. These last two differences favor substitution by rare-earth antisite defects in Nb222M-10 over Nb123-7. The first difference is ameliorated by the formation of anti-structure defects, instead of isolated Pr_{Sr} and nearby antichain oxygen.

Antistructure defect

Since an examination of the crystal-structure of Pr222Nb-10 reveals a lack of space for interstitial O^{-Z} with $Z>1$, and a lack of vacant antichain sites, another way to achieve local charge-balance is needed. We propose that the pair-breaking defect of Pr222Nb-10 is not isolated Pr_{Sr}, but the paired *antistructure defect* (Pr_{Sr},Sr_{Pr}), which is a neutral, pair-breaking defect in which Pr and Sr exchange sites. The self-consistent bond/charge method,[62] when applied to this defect, predicts charges of ${Pr_{Sr}}^{+3}$ and ${Sr_{Pr}}^{+2}$ and potentials at the (original) Sr and Pr sites of -19.5 V and -37.0 V.[51] Exchange of Sr and Pr alters the Sr-site Madelung potential sufficiently to ionize the defect's Pr to Pr^{+3}, while not raising any other Pr-site Pr to Pr^{+4}. Clearly, observation of this anti-structure defect would provide extremely strong confirmation of our model.

D. Primary limitation on T_c

In a cuprate-plane model, the primary limitation on T_c is supplied by limits to the doping of the cuprate-planes by charge-reservoir holes. This suggests that doping experiments on R222M-10 homologues should be able to increase T_c significantly, or at least alter T_c. Such experiments, especially with doping by n-type dopants such as Th, should also cause R122M-8 to superconduct, if the cuprate-planes are indeed the primary elements of superconductivity.[102] As advocates of the charge-reservoir oxygen model, we doubt that Th doping of $R_{2-z}Th_zSr_2Cu_2MO_8$ will produce n-type superconductivity.

V. OTHER SUPERCONDUCTORS

For completeness, in this section we briefly review how our viewpoint affects the interpretation of data for other high-temperature superconductors.

A. $La_{2-\beta}Sr_\beta CuO_4$

$La_{2-\beta}Sr_\beta CuO_4$ has the T crystal structure, which differs from the T' structure of $Nd_{2-z}Ce_zCuO_4$ (Nd21-4) in that the (empty) interstitial sites of the T' structure are occupied by oxygen ions in the T structure, while the T' oxygen sites become (empty) interstitial sites of T.

$La_{2-\beta}Sr_\beta CuO_4$ conduction is indisputably p-type, both from thermopower and Hall measurements,[121] although its cuprate-planes are n-type.[92,109,122] Thus, it appears that the cuprate-planes are not the loci of primary superconductivity in $La_{2-\beta}Sr_\beta CuO_4$.

The widely accepted positive sign of the charge carriers in $La_{2-\beta}Sr_\beta CuO_4$ is to be contrasted with the situation in Nd21-4 and its homologues, where the sign of the carriers is controversial,[111] with a majority of authors following the original suggestion of Tokura *et al.*[27] that electrons carry the charge in the Nd21-4 homologues. However, the Nd21-4 homologue fabricated with the most careful oxygen control is $Pr_{2-z}Ce_zCuO_4$,[24] and the evidence is strong that this robust superconductor is p-type. Thus, in our opinion, the best evidence is that both $La_{2-\beta}Sr_\beta CuO_4$ and $Pr_{2-z}Ce_zCuO_4$ and its homologues are p-type superconductors, and that $La_{2-\beta}Sr_\beta CuO_4$ is certainly not a cuprate-plane superconductor. For $Pr_{2-z}Ce_zCuO_4$ to be p-type, the material must be doped by an additional ion other than Ce—in this case, by interstitial oxygen, which supplies the holes.[62]

Other evidence supporting this viewpoint is provided by pair-breaking by Ni replacing Cu in the cuprate-planes of both $La_{2-\beta}Sr_\beta CuO_4$ and Nd21-4.[54] Using Zn doping of the same sites as a control, the data show clearly that Ni and Zn scatter the same in $La_{2-\beta}Sr_\beta CuO_4$, where the interstitial oxygen is more than a nearest-neighbor distance from the impurity site. In contrast, Ni substituting for Cu in Nd21-4 is a stronger scatterer than Zn (BCS-like), and the interstitial oxygen is directly bonded to the impurity. Our interpretation of these facts is that in both materials the supercurrent passes through the interstitial sites, but only in Nd21-4 is the interstitial site sufficiently close to the magnetic Ni for the Cooper-pair holes to be spin-flip scattered by the impurity's short-range exchange interaction. Thus both $La_{2-\beta}Sr_{\beta}CuO_4$ (T) and the Nd21-4 (T') homologues fit into the picture of charge-reservoir superconductivity.

The T^* structure, which has half of the unit-cell being T and the other half being T', has the properties of both structures, and so offers little unique information for understanding superconductivity.

B. BSCCO, $Tl_2Ba_2CaCu_2O_8$, and $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$ compounds

The microwave radiation spectra[123] of BSCCO ($Bi_2Sr_2CaCu_2O_8$) show features consistent with the charge-reservoir model, but not with a cuprate-plane picture, when analyzed carefully.[124]

The dopant oxygen in $Tl_2Ba_2CaCu_2O_8$ is confined to a volume so small that the oxygen must be nearly neutral (not O^{-2}) and must have almost two holes attached to it. If the holes are attached to the interstitial dopant oxygen, they clearly have not migrated to the cuprate-planes. This suggests that the primary superconducting condensate is in the charge-reservoirs of this material as well.[125]

The application of physical hydrostatic pressure to the $n=1$ Hg compound $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$,[125] causes T_c to increase, and the charge-transfer from the Hg-layer charge-reservoirs to the cuprate-planes to become more negative, not more positive, as required in a cuprate-plane model.[125] The charge transfer varies virtually the same with the number of cuprate-planes in the crystal structure, as with pressure p.[125] These results suggest that the data may be better described with the charge-reservoir oxygen picture than with the cuprate-plane picture.

C. Selected experiments

For $M=$Nb, Ta, or Ti, there have been no experiments to date that even claim to provide independent evidence *for* cuprate-plane superconductivity in Nd222M-10 and its homologues. Therefore the disputes and controversies surrounding the nature of superconductivity in other materials have little *direct* bearing on the Nd222M-10 class of materials. Nevertheless, we address here a few of the measurements often cited as evidence of *primary* cuprate-plane superconductivity, recognizing that some materials such as Y123-7 exhibit superconductivity in *both* the charge-reservoirs and the cuprate-planes, with the *primary* superconducting layers best determined by impurities which produce Cooper-pair-breaking.[99,91]

Optical conductivity experiments offer insight into the location of the primary superconducting condensate, from a combination of anisotropy of the spectra and oscillator-strength sum rules. Using such methods, Basov *et al.*[126] have shown that over half of the superconducting condensate in Y123-7 is in the charge reservoirs. In $YBa_2Cu_4O_8$, over 75% of the condensate is in the reservoirs. Thus it appears that the *primary* superconductivity of these two compounds is in the charge-reservoirs, not in the cuprate-planes.

Recently Srikanth *et al.*[127] have cautiously interpreted their surface impedance data to suggest that Y123-7 has *two* order parameters: one that is s-like and associated with 90 K superconductivity in the charge reservoir regions, and another that may be d-like, attributable to pairing in the cuprate-planes, and associated with a lower critical temperature (~60 K). If this is correct, then many claims for *primary* cuprate-plane superconductivity need to be re-evaluated.

For example, photoemission experiments,[128] which measure energy-band-dispersion and Fermi surfaces, have not been able to *locate* the superconducting layers directly without supplementary information; and photoemission measurements would find it difficult to determine which of two layers provides the *primary* superconductivity. Furthermore, such experiments have only been performed on a limited number of high-temperature superconductors: most notably on Y123-7[129] and BSCCO,[130,131] and to a lesser extent on $La_{2-\beta}Sr_{\beta}CuO_4$ and the Nd21-4 homologues.[84] These experiments are also remarkably surface-sensitive, with typical electron escape depths being about 17 Å. Often the materials studied (which are inhomogeneous, especially at the surface) cleave at the charge-reservoirs, implying that the cuprate-planes are buried. What is worse, especially in the case of BSCCO, it has been argued that the local density of states varies by several orders of magnitude, even within the small 17 Å escape depth,[132] compounding any analysis and invalidating assumptions concerning the constancy of the matrix elements within the escape depth. Therefore it is perhaps better to examine the data for scanning tunneling microscopy/spectroscopy (STM/S), which provides spectra that are akin to Fourier transforms of what photoemission measures.[133–137] The STM/S measurements are extremely sensitive to the layer of atoms at the very surface, and detect evidence of superconductivity accompanying images of the topmost Bi-O layers. The record to date for STM/S detection below the surface is provided by images of subsurface InSb (110),[138] and so claims to have demonstrated that the cuprate-planes superconduct[132] assume two heroic achievements: (i) imaging of yet a third subsurface layer at a record depth below the surface, and (ii) evidence that the cuprate-plane layer is characterized by a local density of states that is several orders of magnitude larger than those at the surface and first sub-surface layers.

Finally, nuclear magnetic resonance (NMR) measures primarily Knight shifts and spin-relaxation rates, but the Hebel-Slichter peaks normally detected in low-temperature superconductors are absent in high-temperature superconductors leaving unanswered many questions about how to interpret data.[42] However, it has been known for some time that NMR studies of $YBa_2Cu_3O_7$ find that the charge-reservoir layers (namely, atoms in the neighborhood of the Cu of the Cu-O chains) exhibit conventional, BCS-like s-wave superconductivity.[139]

VI. SUMMARY

We look forward to experimental confirmation of the many predictions in this article. The fact that the charge-reservoir oxygen model successfully indicates that the critical temperature will be $T_c \approx 30$ K, at a time when the cuprate-plane picture is under assault from a number of experiments, suggests that further studies of $R222M$-10 may hold some of the keys to understanding high-temperature superconductivity.

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