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Comparison of bulk R_{2-z}Ce$_z$CuO$_4$ with superlattice R_{2-z}Ce$_z$CuO$_4$/SrO/NbO$_2$/SrO/CuO$_2$

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Bulk R_{2-z}Ce$_z$CuO$_4$ compounds superconduct for trivalent ions R = Pr, Nd, Sm, and Eu, but not for Gd or for Cm (with Th replacing Ce). R_{2-z}Ce$_z$Sr$_2$Cu$_2$NbO$_{10}$ is a natural superlattice of R_{2-z}Ce$_z$CuO$_4$ and the layers SrO/NbO$_2$/SrO/CuO$_2$; it exhibits bulk superconductivity for R = Nd, Sm, Eu, and Gd, but not for R = Pr. These differences imply that the superconducting regions in the bulk and in the superlattice must be different, and not both cuprate planes. The primary superconductivity is assigned to interstitial oxygen and Nd-O layers in the bulk and to Sr-O layers in the superlattice. [S0163-1829(99)05741-0]

I. RARE-EARTH COMPOUNDS

Comparative studies of the properties of different but similar high-temperature superconductors offer opportunities to learn details of the mechanisms of superconductivity that might otherwise be obscured. Classes of materials that have proven especially illuminating are the superconducting homologues containing different rare-earth ions, such as R_{2-z}Ce$_z$CuO$_4$ (R21-4) (R = rare earth) (Refs. 1–6) or RBa$_2$Cu$_3$O$_7$ (R123-7) (Refs. 7–17). The trivalent rare-earth ions all have about the same radius, ~1 Å, ranging from 0.85 Å for Lu^{3+} to 1.14 Å for La^{3+},[18] and exhibit the famous but small lanthanide contraction as they become heavier. Chemically the trivalent ions are all similar, having Xe-like outer shells within which lie 4f electronic shells of radii ~0.4 Å. These 4f shells are responsible for the ions' magnetic moments, and they can be thought of as point magnets with the different rare-earth ions having different magnetic moments. Therefore, changing the rare earths changes the magnetism of the ions but only slightly changes the size; otherwise, to an excellent approximation, there is no change.

II. NATURAL SUPERLATTICE COMPOUNDS

A relatively unexplored area of investigation involves the ''natural superlattices,'' materials such as R_{2-z}Ce$_z$Sr$_2$Cu$_2$NbO$_{10}$ (R222Nb-10),[19–24] which are superlattices of R21-4 and the oxide layers SrO/NbO$_2$/SrO/CuO$_2$ (see Fig. 1). Although there are slight differences in bond lengths, the oxide layers appear not to greatly influence the superconductivity: For example, with R = Nd, the Nd21-4 layers in Nd222Nb-10 appear to be otherwise structurally identical to those of the bulk superconductor Nd21-4; the main difference seems to be the continuously variable Ce-doping level z, which is optimal for $z \approx 0.15$ in Nd21-4 and $z \approx 0.5$ in Nd222Nb-10, and which might conceivably be different in order to maintain a specific hole density at some location. Thus one is led to believe that the superconducting layers in both materials are the same: a subset of the layers in Nd21-4, perhaps even the cuprate planes.

A. Different superconducting units

However, if the superconducting layers are *the same* in both Nd21-4 and the natural superlattice material Nd222Nb-10, then *replacement of Nd by another rare-earth ion (such as Gd) must render either both or neither Gd21-4 and Gd222Nb-10 superconducting—with similar results for Pr replacing Nd*. In fact this does not happen for either Gd or Pr (although it does happen for Sm and Eu): Gd21-4 does not superconduct,[25] while Gd222Nb-10 does,[21,22] and Pr21-4 does superconduct,[2] while Pr222Nb-10 does not exhibit bulk superconductivity.[21,22,26]

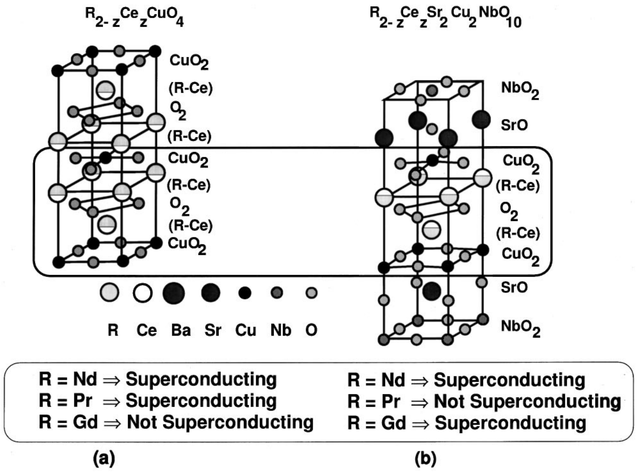

FIG. 1. Crystal structures of (a) R_{2-z}Ce$_z$CuO$_4$ (with z typically ≈0.15), where R is a rare-earth ion, and (b) R_{2-z}Ce$_z$Sr$_2$Cu$_2$NbO$_{10}$ (with z typically ≈0.5), which is a natural superlattice of R_{2-z}Ce$_z$CuO$_4$ and the oxide layers SrO/NbO$_2$/SrO/CuO$_2$. The boxed parts of the structures are common to both. For the trivalent rare-earth ions Nd, Pr, and Gd, structure (a) superconducts for Nd and Pr, but not Gd, while structure (b) exhibits bulk superconductivity for Nd and Gd, but not Pr. Recently, we have shown that Pr222Nb-10 exhibits *granular* superconductivity, as discussed in the text. The fact that both (a) and (b) do not have the same properties for R = Nd, Pr, and Gd indicates that the superconducting structural region is necessarily different in the two sets of homologues.

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This is strong evidence that the communal geometrical unit, namely either the cuprate planes, the Nd21-4 unit cell, or whatever universal structural entity is supposedly hosting the primary superconducting condensate[27] in Nd21-4 is *different* from the corresponding superconducting entity in Nd222Nb-10. It also is an important clue concerning the origin of high-temperature superconductivity. If the unifying structural superconducting entity in both compounds is the same when the rare earth is Nd, then making the same change to both compounds Nd21-4 and Nd222Nb-10, Nd→Gd or Nd→Pr, must produce compounds that either both superconduct or both do not superconduct—or else the unifying structural superconducting entities were not the same to begin with. Clearly, whatever is superconducting in Nd21-4 is different from whatever is superconducting in Nd222Nb-10. In particular, the failures of Gd21-4 and Pr222Nb-10 to exhibit bulk superconductivity must be either due to defects, or else the cuprate planes cannot be the primary superconducting layers in both the R21-4 and the R222Nb-10 compounds.

B. Superconducting Sr-O planes

We propose that the superconducting entity involves the R-O layers and interstitial oxygen (near the face center of the R plane) in R21-4,[28] but is associated with the Sr-O layers of R222Nb-10. The reasons for these assignments are: (i) These are the locations of the holes or the hypocharged oxygen (O^{-Z} with $Z<2$, as determined by the bond-valence-sum method[29]), and we expect the primary superconducting condensate to be where the holes are; and (ii) these are the layers that either do not contain pair-breaking magnetic moments (as in R222Nb-10), or that contain only moments that are rendered impotent for pair breaking by the crystal-field splitting (as for R21-4, with R=Pr, Nd, Sm, and Eu).[28,30] It is certainly true in conventional superconductors that the supercurrent is where the carriers are and resides in regions lacking pair-breaking magnetic moments. We think that these principles carry over to high-temperature superconductors much more easily than some of the hypotheses that have been proposed assigning the supercurrent to cuprate planes.[31,32] Evidence supporting this notion includes (i) $Ba_{1-a}K_aBiO_3$ is a 32-K superconductor with most of the properties of the superconducting cuprates,[33] except no cuprate planes; (ii) YSr_2RuO_6 doped with Cu is also reported to be an 80-K superconductor,[34] despite having no cuprate planes; and (iii) Cu-less WO_3 doped with Na is a 90-K superconductor.[35] Moreover, $LaBa_2Cu_2NbO_8$ does have cuprate planes but does not superconduct.[36] Therefore, cuprate planes are neither necessary nor sufficient for high-temperature superconductivity, and so there is no rational basis for assigning them a central role in the theory.

C. Additional evidence

Further evidence that the superconductivity of the R21-4 and R222Nb-10 homologues originates in different parts of the crystal structures is provided by different crystal-field and size effects.

(i) The introduction of an $L=0$ ion (Gd^{3+} or Cm^{3+}) to a rare-earth site quenches the superconductivity in the R21-4 homologues,[1,37,38] but not in the R222Nb-10 structures.[21,22] This difference is attributed to Cooper pair breaking by the rare-earth magnetic moments, which is allowed for $L=0$ but forbidden by crystal-field splitting of $L\neq 0$ ions in the R21-4 structures.[30,39] The importance of crystal-field splitting in R21-4 homologues but not in R222Nb-10 structures (although the fields near the rare-earth sites should be virtually the same) implies that the superconducting condensate is close to the rare-earth in R21-4 but remote in R222Nb-10.

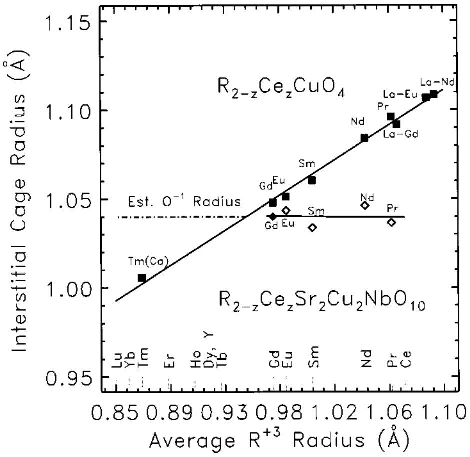

FIG. 2. Inscribed radius of the cage of oxygen ions (in a hard-sphere approximation) surrounding the interstitial oxygen site near the face center of the rare-earth plane in $R_{2-z}Ce_zCuO_4$ (slanted line, open squares) and $R_{2-z}Ce_zSr_2Cu_2NbO_{10}$ (nearly horizontal line, diamonds) versus trivalent rare-earth radius (in Å). The R =Tm datum (Ref. 41) corresponds to Ca doping, not Ce, and so is not constrained by a cage-size effect, as when the dopant is (Ce, interstitial oxygen). The solid diamond for Gd indicates that neutron-diffraction data are not available, but the material superconducts, and so we have assigned the material the average inscribed radius for the class. The data are for R=La-Eu (Ref. 42), La-Nd (Ref. 1), and La-Gd alloys (Ref. 1), and for Gd, Eu, Sm, Nd, and Pr (Ref. 6). The chained line is our estimate of the radius of an O^- ion and lies within 0.01 Å of the radius of O^- interpolated between O^0 and O^{2-}. Note the size effect: none of the $R_{2-z}Ce_zCuO_4$ materials forms with Ce doping or superconducts for trivalent R ions smaller than Gd.

(ii) The mechanism of superconductivity in R21-4 homologues is controversial, with the only self-consistent proposal involving co-doping of Ce by interstitial oxygen.[3,4] In this picture, there is a size effect:[4,28,40] when the cage of ions surrounding the interstitial site becomes too small to contain O^{-1}, the superconductivity must vanish. This size effect, which forbids superconductivity for smaller rare-earth ions than Gd^{+3}, appears to be present in R21-4 materials, but not in R222Nb-10 [Fig. 2 (Refs. 41 and 42)], again indicating that whatever entity is superconducting in R21-4 is different in R222Nb-10.

(iii) The failure of Pr222Nb-10 to exhibit bulk superconductivity[26] is assigned to pair breaking by Pr_{Sr}, analogous to the case of Pr123-7 (Ref. 43), which superconducts only after Pr_{Ba} is minimized.[10,11,26] Again, no comparable effect is observed in Pr21-4.

III. EXPERIMENTAL STATUS

Based on these ideas, (i) Gd21-4 intrinsically cannot superconduct, and (ii) Pr222Nb-10 will produce bulk superconductivity only if the $\mathrm{Pr_{Sr}}$ defects are minimized.

Accordingly, we initiated searches for *granular* superconductivity in both compounds, and found none in Gd21-4 (as expected).[44] In Pr222Nb-10 we found evidence of *granular* superconductivity, together with neutron diffraction data indicating the presence of heavy concentrations of the pair-breaking defect $\mathrm{Pr_{Sr}}$.[26] These observations are fully consistent with the ideas presented here: $\mathrm{Pr_{Sr}}$ is a Cooper-pair breaker, but rare-earth site Pr is not—implying that the primary superconducting condensate[27] cannot be in the cuprate planes, adjacent to the Pr site.

IV. $\mathrm{PrBa_2Cu_3O_7}$ (Pr123-7)

Thus the facts for R222Nb-10 and R21-4 buttress the facts that Pr123-7 superconducts in the ideal crystal structure at a critical temperature approaching ≈90 K, but does not superconduct when significant amounts of Pr occupy Ba sites.[10–17,43,45–47] The facts for Pr123-7 are contrary to the predictions of cuprate-plane theories, but *agree* with the predictions of a theory that places the primary superconductivity in the charge-reservoir layers, not in the cuprate planes.[43,48–50] The reason that the Pr123-7 data are inconsistent with cuprate-plane superconductivity is that they arise from a fundamental asymmetry: Pr on a rare-earth site has no adverse effect on ≈90-K superconductivity, but Pr on a Ba site destroys the superconductivity. If the superconducting condensate lies primarily in the cuprate planes, then a rare-earth site and a Ba site are located almost symmetrically with respect to the cuprate plane in between them (at almost the same distance from the plane). Since Pr has a magnetic moment, it is expected to break Cooper pairs in an adjacent superconducting condensate (Fig. 3). But the magnetic environments on both sides of a cuprate plane are essentially the same, and so the observation of asymmetric pair-breaking behavior, namely, Ba site Pr breaks pairs but rare-earth site Pr does not, is inconsistent with a symmetric magnetic environment—and can be explained only if the primary condensate is not in the cuprate plane, but in the charge-reservoir layer adjacent to the Ba site. Thus one is *forced* to adopt charge-reservoir superconductivity, not only by the many predictions of cuprate-plane theories that failed to be realized, but also by symmetry.

Many other experiments now require p-type charge-reservoir superconductivity as well. We mention only four: (i) In $\mathrm{Pb_2Sr_2Ca_{0.5}}R_{0.5}\mathrm{Cu_3O_8}$ no superconductivity occurs for $R=$Ce or Am, which are tetravalent and so should dope the material n type, while trivalent (p type) $R=$Pr and Tb superconduct—implying that the superconductivity lacks the expected particle-hole-doping symmetry implicit in most cuprate-plane theories. (ii) The chemical trends, both in the critical temperatures T_c and in the amount of Ni or Zn, u_c, required to quench superconductivity in the common high-temperature superconductors, as the cuprate planes become more distant from the charge-reservoir layers,[51–53] indicate very clearly that the primary superconducting condensates lie in the charge-reservoir layers, not in the cuprate planes, (iii) The sizes of the (interstitial) dopant oxygen ions in superconductors such as $\mathrm{Tl_2Ba_2CaCu_2O_8}$ indicate that they still have most of their holes attached, indicating that the holes have not left the doping layer for the cuprate planes.[54] (iv) By starting with the inconsistency that Ce in isolation cannot account for the doping in Nd21-4 and its homologues, one is naturally led to a model of doping by (Ce, interstitial O) pairs, p-type superconductivity, a lack of crystal-field splitting for the Gd and Cm homologues, and a size effect on superconductivity for rare-earth ions smaller than $\mathrm{Gd^{+3}}$ (Refs. 28 and 40)—all of which are observed.

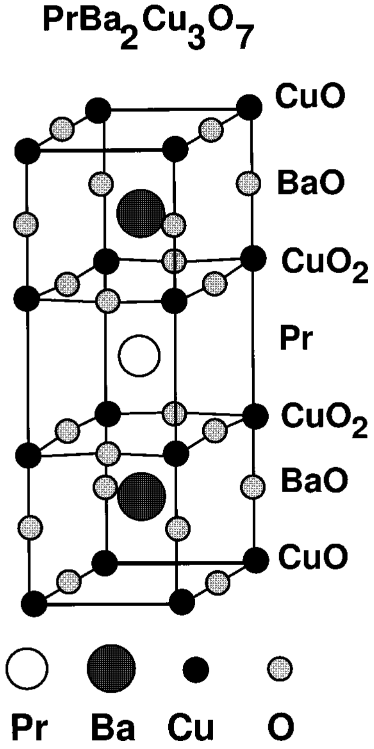

FIG. 3. Crystal structure of $\mathrm{PrBa_2Cu_3O_7}$.

V. SUMMARY

The evidence speaks for itself: the structural units responsible for superconductivity in $R_{2-z}\mathrm{Ce}_z\mathrm{CuO_4}$ and $R_{2-z}\mathrm{Ce}_z\mathrm{Sr_2Cu_2NbO_{10}}$ are different. The widely accepted conventional cuprate-plane picture of high-temperature superconductivity requires revision.

ACKNOWLEDGMENTS

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