

Evidence that all high-temperature superconductors are p -type

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The ground charge state of Ce substituting for Nd^{+3} in Nd_2CuO_4 is usually assumed to be Ce^{+4} , indicating that Ce is a donor which causes $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ to be an n -type superconductor. Using the self-consistent bond/charge method, we show that the Ce ground state is Ce^{+3} , not Ce^{+4} , in *ideal* Nd_2CuO_4 , implying that monatomic Ce dopants are isoelectronic centers, not n -type donors. The observed Ce doping of $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ can be understood if an interstitial oxygen binds to the Ce, elevating its charge state to Ce^{+4} . This is a paired defect of Ce and oxygen, which dopes the host p -type, not n -type, because of oxygen's $2p$ holes. The condition that the interstitial oxygen does dope the host p -type translates into an approximate steric constraint that the ionic radius of the rare-earth ion R^{+3} must exceed that of Tb^{+3} for $R_{2-z}\text{Ce}_z\text{CuO}_4$ to superconduct. A similar situation occurs for the infinite-layer material $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$, where the Nd dopant is isoelectronic Nd^{+2} , not donor Nd^{+3} as assumed, unless an extra oxygen is adjacent to the Nd. The data are reviewed in light of these results, and show no convincing evidence either of particle-hole symmetry in doping, or of n -type doping of any high-temperature superconductor. Instead they hint that the superconductivity is associated with oxygen, rather than with any particle-hole-symmetric cuprate-plane phenomenon. [S0163-1829(97)01209-5]

I. INTRODUCTION

An important issue concerning high-temperature superconductivity is whether all such superconductors are p -type or not. The models that rely on oxygen as the generator of superconductivity, whether cuprate-plane oxygen^{1,2} or charge-reservoir oxygen,³ assume that the current carriers are the $2p$ holes of oxygen. Such models would require major modification to be compatible with n -type superconductivity by electrons: there is no particle-hole symmetry in an oxygen model of superconductivity, because O^{-1} and O^{-2} naturally form in ceramics much more easily than O^{+1} or O^{+2} . The more traditional models based on cuprate planes⁴ generally do not provide a clear and specific picture of the assumed remote source of carriers, but merely treat the source as a parameter to be specified independently of the superconductivity, allowing the carriers to be either electrons or holes. The models themselves typically have particle-hole symmetry, with the *theoretical* cuprate planes that generate the superconductivity being equally compatible with n -type and p -type carriers. To our knowledge, no single compound has exhibited both n -type and p -type high-temperature superconductivity with different dopants, although this doping behavior is expected of theories with particle-hole symmetry. Moreover, all assignments of n -type superconductivity are controversial, including that for the most studied candidate, $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$. The evidence is such that one can credibly argue that *no* high-temperature superconductor exhibits the particle-hole symmetry common to so many theories, both because none of the main candidates for n -type superconductivity also exhibits p -type behavior with another dopant and also because all the n -type candidates themselves are controversial.

The main candidates for n -type superconductivity are $R_{2-z}\text{Ce}_z\text{CuO}_4$, for the lighter, magnetic rare earths $R=\text{Pr}$, Nd , Sm , and Eu ,⁵⁻⁸ and the infinite-layer compounds $\text{Sr}_{1-v}\text{R}_v\text{CuO}_2$ for $R=\text{La}$, Pr , Nd , Sm , Gd , and Y .⁹⁻¹² However there is substantial evidence that defects play a central role in infinite-layer superconductivity,¹³ and the case for n -type behavior is rather weak. For example, although $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$'s chemical formula suggests n -type doping,¹² Smith *et al.* found the Hall coefficient of $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$ to be *positive*, normally interpreted as strong evidence of p -type superconductivity. Therefore, except to make a few comments near the end of this paper about the infinite-layer materials, we shall restrict our attention to materials which assume the T' crystal structure, namely homologues of Nd_2CuO_4 (Fig. 1).

In addition to the Ce-doped compounds $R_{2-z}\text{Ce}_z\text{CuO}_4$ with $R=\text{Pr}$, Nd , Sm , and Eu , three Th-doped homologues also superconduct, with Th^{+4} assuming the role of Ce^{+4} : $\text{Pr}_{2-z}\text{Th}_z\text{CuO}_4$, $\text{Nd}_{2-z}\text{Th}_z\text{CuO}_4$, and $\text{Sm}_{2-z}\text{Th}_z\text{CuO}_4$ (with $T_c \approx 2$ K).¹⁴ A closely related material is Ca-doped $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$,⁹ which exhibits the T' crystal structure of $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, is p -type, and superconducts.¹⁵ In all of these superconductors, the optimal doping composition z is typically in the range 0.13–0.17. Except for $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$, all of these compounds that superconduct are thought to be n -type electron superconductors for the same reasons that $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ is. Six closely related materials, which have been fabricated in the T' crystal structure but do not superconduct, are Ce-doped $\text{Gd}_{2-z}\text{Ce}_z\text{CuO}_4$ (Refs. 5–8 and 14) and $\text{LaGd}_{1-z}\text{Ce}_z\text{CuO}_4$,¹⁶ Th-doped $\text{Eu}_{2-z}\text{Th}_z\text{CuO}_4$ and $\text{Gd}_{2-z}\text{Th}_z\text{CuO}_4$,¹⁴ and Ca-doped $\text{Gd}_{2-z}\text{Ca}_z\text{CuO}_4$ and $\text{Dy}_{2-z}\text{Ca}_z\text{CuO}_4$.⁹ A number of compounds, including $\text{Nd}_{2-z-a}\text{Ce}_z\text{R}_a\text{CuO}_4$, for $R=\text{Gd}$, Y , and La , have also been

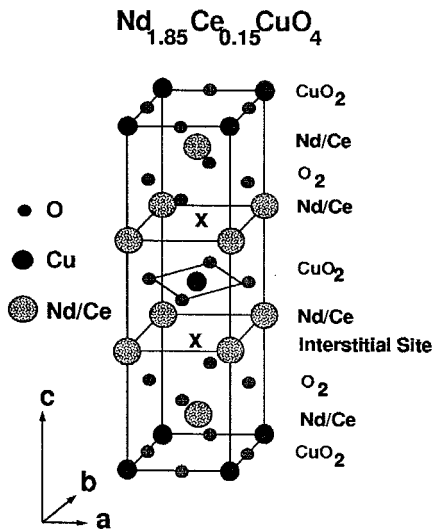


FIG. 1. Crystal structure of (ideal) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ in the T' structure. The approximate possible locations of any (extra) interstitial oxygen ion are denoted "X". When Ce substitutes for Nd, atoms move slightly from their ideal sites.

studied,⁸ with Gd generally being unfavorable to superconductivity.

The main purpose of this paper is to contribute to the discussion of whether the prototypical n -type superconductor, $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, is actually n -type or if it is p -type.

II. IS $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ n -TYPE?

The n -type characterization of $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ has been controversial: (i) Mangelschots *et al.*¹⁷ observed positive normal-state thermopowers in $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ samples which superconducted at lower temperatures. The sign of the thermopower is an indicator of the sign of the charge carrier (at least for a single-band free-electron gas undergoing energy-independent scattering¹⁸). (ii) Jiang *et al.*¹⁹ concluded that $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$'s transport has multiband character, with contributions from both electrons and holes, and Mao *et al.*²⁰ observed a virtually symmetric current-voltage characteristic for a heterostructure composed of indisputably p -type $\text{YBa}_2\text{Cu}_3\text{O}_7$ with purportedly n -type $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$. (One might have expected some evidence of a p - n junction to remain even though the doping levels of these materials are high by semiconductor standards.)

A. Charge state of Ce

Completely absent from previous discussions of the n -type or p -type character of a dopant such as Ce is the question, "In $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, is Ce^{+3} or Ce^{+4} the ground state of the ion?" Obviously, if the ground state of Ce in Nd_2CuO_4 is Ce^{+3} , it does not dope its host n -type; Ce^{+3} merely replaces Nd^{+3} , and is an isoelectronic center rather than the expected n -type donor. An unexpected doping character of an impurity is common in semiconductors, where, for example, oxygen replacing P in GaP is not a donor (as expected), but instead is neither a donor nor an acceptor, tending to make the GaP semi-insulating by virtue of a deep electron and hole trap oxygen produces in the band gap.²¹ It

is well known in semiconductor physics that the doping character of an impurity depends on its host. For example, in PbTe, anion-site In is a donor, but in SnTe the same defect is an acceptor.²² A similar situation occurs in superconductors, where one cannot simply guess that an impurity is a donor because it sometimes assumes a particular charge state, as in the case of Ce^{+4} . Indeed, we shall present evidence that Ce doping of ideal $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ leads to the formation of the isoelectronic defect Ce^{+3} , not the donor Ce^{+4} —namely that *Nd-site monatomic Ce does not liberate its fourth electron and dope (ideal) Nd_2CuO_4 n -type*, as is widely assumed.

B. The actual dopant is interstitial oxygen paired with Ce

We propose that Ce doping normally results in formation of a (*Ce, interstitial-oxygen pair*) consisting of substitutional Ce on a Nd site (actually slightly distorted from the ideal Nd site) and an adjacent interstitial oxygen (Fig. 1). Such interstitials have been reported in various experiments,^{17,23–26} and imply inhomogeneous superconductivity.^{27,28} For the Madelung potential at a Ce site to reach the ionization potential for Ce^{+4} , there must be an interstitial oxygen adjacent to the Ce and bound to it. Thus the dopant is not actually monatomic Ce, but *Ce plus oxygen*, and this paired defect ideally²⁹ liberates a net of one hole: one electron as Ce undergoes the transition $\text{Ce}^{+3} \rightarrow \text{Ce}^{+4}$ plus two holes as oxygen becomes O^{-2} . Thus the ideal pair is a *net p -type dopant, liberating one hole, not one electron*.

C. The self-consistent bond/charge approach

In attempting to determine the ground state of monatomic Ce in Nd_2CuO_4 , we first refer to an early self-consistent-field local-density-approximation calculation for the electronic structure of T -crystal-structure $\text{La}_{2-\beta}\text{Sr}_\beta\text{CuO}_4$ with $\beta=0.0, 0.5$, and 1.0 , implemented using the spin-polarized pseudofunction method.³⁰ That calculation produced the following significant results: (i) the holes of the doped material were predicted to lie in the $\text{La}_{1-(\beta/2)}\text{Sr}_{(\beta/2)}\text{O}$ layers, not in the cuprate planes; (ii) the predicted hole location of that theory is in excellent agreement with both the recently developed self-consistent bond/charge model and with recent measurements,^{31,32} (iii) the doping ($\beta \neq 0$) does not alter the band structure much, but does alter the Fermi energy somewhat—an amount of the same order as is assumed in a rigid-band approximation; (iv) although no comparable calculations for $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ were executed using the pseudofunction method, other local-density calculations³³ reported that the electronic structures of Nd_2CuO_4 and La_2CuO_4 near the Fermi surface are extremely similar; and (v) the calculated magnetic moment on the Cu in La_2CuO_4 was localized and in excellent agreement with the measured value.³⁰ The result that the holes lie in the (La, Sr)-O layers is the opposite of what was once widely assumed: that the holes transferred from the (La, Sr)-O charge-reservoir layers and doped the cuprate planes p -type. However, the cuprate planes in $\text{La}_{2-\beta}\text{Sr}_\beta\text{CuO}_4$ are now known to be n -type,^{31,32} and the p -type hole-doped regions of the crystal structure are the (La, Sr)-O layers. Only these p -type (La, Sr)-O regions (and not the n -type cuprate planes) can produce p -type superconductivity.

TABLE I. Computed ionic charges (in units of $|e|$), magnitudes of Madelung potentials (in V), and ionization potentials IP (in V) (Ref. 37) for ideal $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ (with $z=0.15$), and for the ideal infinite-layer material $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$ (with $v=0.08$). The numbers in parentheses with the ionization potentials are the charges of the final states of ionization. The ionization potentials (in V) to the R^{+3} charge state are, for $R=\text{La, Nd, Pr, Sm, Gd, and Y}$, 19.2, 22.1, 21.6, 23.4, 20.6, and 20.5, respectively. When (Ce, interstitial oxygen) pairs are introduced into $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, the Madelung potential at the Ce site becomes sufficient to ionize Ce to Ce^{+4} (>36.8 V). The charge on the interstitial oxygen is $-1.16|e|$, both from the volume of the oxygen cage containing it, and from the bond-valence sum method (Refs. 39–42), provided the Cu ion which has the interstitial at its apex is displaced away from the interstitial by the experimentally required distance of between 0.5 and 1.0 Å (Ref. 24). A displacement of ~ 0.5 Å meets both the steric and charge constraints. The Ce also relaxes ~ 0.2 Å away from its adjacent cuprate plane (Ref. 25).

| Ion | $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ | | | $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$ | |
|-------------------------|--|-----------|--------------------|--|-----------|
| | Charge | Potential | IP | Charge | Potential |
| Nd | +3.09 | -29.1 | 22.1(+3), 40.4(+4) | +2.14 | -16.6 |
| Ce | +3.23 | -29.1 | 20.2(+3), 36.8(+4) | | |
| Cu | +1.84 | -19.3 | 20.3(+2), 36.3(+3) | +1.81 | -18.7 |
| Sr | | | 11.0(+2), 42.9(+3) | +2.14 | -16.7 |
| O (cuprate plane) | -1.82 | +23.3 | | -1.98 | +25.2 |
| O (O_2 layer) | -2.21 | +23.7 | | | |

The success of the pseudofunction electronic-structure calculations for $\text{La}_{2-\beta}\text{Sr}_\beta\text{CuO}_4$, combined with various successes of the easier-to-implement self-consistent bond/charge theory and the similarity of Nd_2CuO_4 to La_2CuO_4 , provides justification for applying the self-consistent bond/charge approach to the problem of Ce doping of Nd_2CuO_4 : (i) The effective charge Q_σ on the σ th ion is computed from its bond lengths $|\mathbf{r}_{\sigma',\sigma}|$ using the phenomenological bond-valence-sum method.^{34,35} With bond lengths $|\mathbf{r}_{\sigma',\sigma}|$, the relationship between the bond lengths and charges is

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

where we have $B=0.37$ Å, $|e|$ is the proton's charge, the sum is over all ions σ' directly bonded to the σ th ion,³⁶ $w_{\sigma'}$ is the probability that the site is occupied by a particular atom of type σ' , and $|\mathbf{r}_{\sigma',\sigma}|$ is the bond length between the atom on site σ and an atom of type σ' at one of its neighboring sites. The parameters R_σ are extracted from known bond lengths of many chemical compounds and are tabulated in Ref. 34. (ii) With these charges, the Madelung potential $V(\mathbf{r}_\sigma)$ at each site \mathbf{r}_σ is computed by summing over all ions ν :

$$V(\mathbf{r}_\sigma) = \sum_\nu Q_\nu / |\mathbf{r}_\sigma - \mathbf{r}_\nu|.$$

(iii) The Madelung potential is compared with the ionization potentials of the ion on that site,³⁷ to determine if the potential is strong enough to ionize the ion to the expected charge state.³⁸ If the magnitude of the Madelung potential is weaker than the ionization potential by more than ~ 1 V, then in all likelihood the ion on that site is not ionized to the higher charge state. Only if the various ionic charges obtained from the bond lengths are nearly equal to the charges deduced from the ionization potentials do we accept the computed charge states. Otherwise we start over, selecting different integral ionic charges as input for the bond-length analyses, until we find a self-consistent solution.

I. Application to $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$

We applied this method to $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, and found that the charge state of Ce is $\text{Ce}^{+3.23}$, and that the magnitude of the Madelung potential at the Ce site is ~ 29.1 V, compared with 36.8 V required to ionize Ce to Ce^{+4} . See Table I; (Refs. 37, 39–42). This ~ 7.7 V difference is so large that it is unnecessary to do a more sophisticated calculation, especially since both the computed charge ($+3.23|e|$) and the potential (-29 V) self-consistently indicated that, at the Ce site, Ce is Ce^{+3} , is an isoelectronic center, and is not a dopant of any type. In particular, Ce is not an n -type dopant. In ideal Nd_2CuO_4 , Ce replacing Nd is in the charge-state Ce^{+3} , and does not account for the observed superconductivity.

Experimentally, Ce in Nd_2CuO_4 yields superconductivity, each Ce donates about one electron to a Cu-related band while leaving the typical Cu ion in the Cu^{+2} ionic state,⁴³ and Ce is nonmagnetic¹⁴ (i.e., closed-shell Ce^{+4}). The only way that the electrostatic point-ion potential at a Ce site can be made large enough to ionize Ce to Ce^{+4} is if an additional anion is placed close to the site—an oxygen interstitial. There is space available in the unrelaxed lattice to accommodate hypocharged oxygen (not fully charged to O^{-2}) at or near the ideal, unrelaxed interstitial site, which is at the face-center of the Nd plane and ≈ 2.3 Å distant from the nearest Ce site.^{39–41} This oxygen could meet the steric constraints even without local lattice relaxation if its charge $-Z_I|e|$ were such that $Z_I < 1.16$,⁴⁴ making the interstitial oxygen small enough to fit in the cage of surrounding oxygen ions. This interstitial charge would contribute an additional potential of magnitude $(6.5 Z_I)$ V at the Ce site—compared with the 7.7 V needed to achieve Ce^{+4} . Thus, for reasonable interstitial charges $-Z_I|e|$ (and with reasonable lattice relaxation),^{24,25} the potential at the Ce site is likely to be strong enough to ionize Ce to Ce^{+4} . Likewise, the charge at the Ce site will increase by $\sim |e|$ due to the inclusion of the bond between the interstitial and the Ce, while the Cu charge will remain near $+2|e|$. Thus the Ce charge assumes a value around $+4|e|$, making the (Ce, interstitial-oxygen) defect a

dopant that self-consistently satisfies the conditions of the bond/charge method, with Ce^{+4} . We executed calculations for $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ containing interstitial oxygen, and found that this is indeed the case.⁴⁵

Thus the self-consistent bond/charge method offers two possible solutions for $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$: (i) Ce is isolated, in the charge-state Ce^{+3} , and electrically inactive, neither doping n -type nor causing superconductivity; and (ii) Ce is accompanied by interstitial oxygen, contributes its fourth electron to doping, and is Ce^{+4} . The Ce^{+4} solution is the one relevant to superconductivity in $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, but leaves the material p -type, because interstitial (initially neutral) oxygen ideally has two $2p$ holes which it can release.²⁹ In the ideal weak defect-host coupling limit, the dopant is a (Ce, O) pair: ideally $\text{Ce}^{+4}-\text{Nd}^{+3}+e^-+\text{O}^{-2}+2h^+$. Consequently the (Ce, interstitial-oxygen) defect complex can be a net *acceptor*, doping Nd_2CuO_4 p -type. Previous work *assumed* that the Ce^{+4} observed was associated with an *isolated* defect, and thus that Ce's ionized electron doped the cuprate planes n -type.^{23,43,46} The self-consistent bond/charge scheme shows that the relevant defect is not isolated Ce, which is an isoelectronic center and a neutral defect (Ce^{+3}) rather than a donor, as assumed. It also indicates that the defect complex (Ce, interstitial oxygen) produces p -type superconductivity in the vicinity of the interstitial and in the nearby O_2 layer, as discussed in Ref. 31.

III. IMPLICATIONS

Having concluded that Ce in $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ forms a (Ce, interstitial-O) complex that is a p -type dopant, it is straightforward to draw similar conclusions for both the Ce-doped and the Th-doped homologues.

A. Oxygen solubility and interstitial cage size

A major factor governing the occurrence of superconductivity in the $R_2\text{CuO}_4$ homologues is the Ce-induced doping by interstitial oxygen. Therefore the solubility of interstitial oxygen in the cage of surrounding oxygen ions becomes an issue, as does the question of whether the cage is large enough to accommodate an oxygen ion with the required charge. The highest values of the critical temperature are obtained when the superconducting $R_{2-z}\text{Ce}_z\text{CuO}_4$ compounds are fabricated under high pressure,⁴⁷ consistent with the expectation that the solubility of oxygen in the interstitial cage can be increased by pressure.⁴⁸

The size of the interstitial cage determines a condition for p -type doping and superconductivity. The cage of oxygen ions surrounding the interstitial oxygen must be large enough to accommodate a superconductivity-sensitizing interstitial oxygen ion that has acquired a charge $-Z_I|e|$ with $Z_I > 1$, namely an oxygen that has yielded more than one hole to the host (to both compensate the electron from dopant Ce and dope the host p -type). An examination of the crystal structure of $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ reveals that the sphere inscribed in the interstitial cage^{39,40,49} is sterically incapable of containing an oxygen ion of charge $-Z_I|e|$ if $Z_I > 1.16$, assuming an oxygen ionic radius linearly interpolated between those of O^0 and O^{-2} : $(0.65+0.375 Z_I) \text{ \AA}$.⁴⁴ Consequently the range of interstitial oxygen charges compatible with p -type doping

and superconductivity ($1 < Z_I < 1.16$) is small even in $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ and smaller yet for the heavier rare-earth homologues.^{50,51} Since the radius of the inscribed sphere decreases approximately linearly with the decreasing ionic radius⁵² of the trivalent rare-earth ion of the host, the $R_{2-z}\text{Ce}_z\text{CuO}_4$ homologues cease to superconduct once the rare-earth ionic size becomes too small for the interstitial cage to accommodate the required $Z_I > 1$ oxygen ion. From an examination of the lattice constants,⁴⁹ the $Z_I = 1$ condition is met for a rare-earth ionic radius near Tb^{+3} 's, namely, slightly smaller than Gd^{+3} 's. This trend with size is visible in the data: T_c decreases from ≈ 32 K in pressure-fabricated $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ (Ref. 47) (21 K for normal fabrication⁵⁰) to ≈ 7.5 K for $\text{Eu}_{2-z}\text{Ce}_z\text{CuO}_4$,⁵⁰ as the oxygen cage size decreases, and vanishes for $\text{Gd}_{2-z}\text{Ce}_z\text{CuO}_4$ and $R_{2-z}\text{Ce}_z\text{CuO}_4$ with smaller trivalent rare-earth ions R , although the failure of $\text{Gd}_{2-z}\text{Ce}_z\text{CuO}_4$ to superconduct is probably not due to a size effect, but to its total angular momentum $L = 0$.⁵³⁻⁵⁶ For doping by Th^{+4} , a slightly larger dopant than Ce^{+4} , the onset of $R_{2-z}\text{Th}_z\text{CuO}_4$ superconductivity corresponds to a slightly larger trivalent rare-earth radius, between those of Eu^{+3} and Sm^{+3} .¹⁴

B. Particle-hole symmetry

If particle-hole symmetry is valid, and if interstitial oxygen is involved in the doping as we propose, then the Ce^{+4} -doped and Th^{+4} -doped $R_2\text{CuO}_4$ compounds must not *cease* superconducting for R^{+3} smaller than Gd^{+3} (as they do), but must switch to n -type superconductivity, as the interstitial oxygen's charge becomes $Z_I < 1$.

C. Ca-doped Tm_2CuO_4

The Ca-doped $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$ appears to be another manifestation of the p -type $R_2\text{CuO}_4$ compounds¹⁵—except that the Ca doping is by an isolated defect (Ca on a Tm site), rather than by a defect pair (Ce on a rare-earth site, paired with interstitial oxygen). This significant difference between the Ca-doped $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$ and the Ce-doped $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ implies that the p -type doping, not the interstitial oxygen itself, is critical for superconductivity in the $R_2\text{CuO}_4$ compounds.¹⁵ The Ce-doped compound is expected to have roughly one interstitial oxygen ion per Ce, while the interstitial oxygen concentration in the Ca-doped material is likely to be much smaller because there is no strongly positive Ce^{+4} ion attracting the negative oxygen. Thus, we expect that T_c of $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$ should not be depressed by a lack of greater interstitial-oxygen solubility; this appears to be the case for this pressure-fabricated superconductor:⁹ $T_c = 30$ K, compared with 32 K for $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$. Moreover the effect of replacing Cu by Ni and Zn in Ca-doped Tm_2CuO_4 and Ce-doped Nd_2CuO_4 will be rather different: In $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$, less than 1% Ni destroys the superconductivity, while about six times as much Zn is required to accomplish the same effect.⁵⁷ This is because the interstitial oxygen is apical to the impurity site and directly bonded to it, and the supercurrent in $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ passes through this interstitial site. Therefore the superconductivity of $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ senses the adjacent magnetic moment of Ni, and T_c is depressed rapidly by the Cooper pair-breaking effect of that magnetic moment. In contrast, we expect very little interstitial (apical) oxygen in $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$, and

hence any superconducting condensate should primarily occupy the O₂ planes, where the strongly electropositive Ca will insert the holes.³¹ This means that, to a good approximation, the supercurrent, which does not involve interstitial oxygen, will not experience exchange scattering and Cooper pair breaking by Ni on a Cu site (because the distance from the impurity to the nearest hole-carrying oxygen exceeds the range of the exchange scattering)—and hence that Ni and Zn should have similar effects on T_c due to their similar long-ranged scattering potentials. Studies of T_c versus Ni and Zn dopant concentrations u for the two materials should exhibit this dramatic difference: $T_c(u)$ for Ni and Zn should be about the same in superconducting $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$, but $T_c(u)$ for Ni is smaller than for Zn in $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ and vanishes for a considerably smaller value of u .⁵⁷

IV. CONCLUSIONS

Our main conclusion is that isolated Nd-site Ce in ideal $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ is Ce^{+3} and does not provide n -type doping, as widely assumed. Rather, most Ce ions facilitate the formation of an adjacent interstitial oxygen, and the (Ce, interstitial-oxygen) pair causes Ce to ionize to Ce^{+4} , while the oxygen dopes Nd_2CuO_4 net p -type. A dramatic test of this picture would be the demonstration that $T_c(u)$, as a function of Ni or Zn dopant concentration u , would be the same for Ni and Zn in superconducting $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$, which is not the case for Ni- and Zn-doped $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$.⁵⁷

A similar story holds for the infinite-layer compounds that are thought to be n -type. As Table I shows, the predicted ground charge state of Nd on a Sr site in $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$ is

Nd^{+2} , not Nd^{+3} . Thus Nd does not dope $\text{Sr}_{1-v}\text{Nd}_v\text{CuO}_2$ at all, much less n -type, and off-site oxygen or a cation vacancy must be involved in its superconductivity, which must be p -type.

In summary, the analyses presented here indicate that $\text{Nd}_{2-z}\text{Ce}_z\text{CuO}_4$ and its T' -crystal-structure homologues are all p -type. They also suggest that the $\text{Sr}_{1-v}\text{R}_v\text{CuO}_2$ infinite-layer compounds are not doped n -type by isolated rare-earth ions R either, because those ions appear unlikely to achieve the R^{+3} charge state in isolation.

Thus one can propose that there are *no* n -type high-temperature superconductors, which, if true, points toward superconductivity by hypocharged oxygen,⁵⁸ rather than particle-hole-symmetric cuprate-plane superconductivity, as the general cause of high-temperature superconductivity. This, of course, means that Cu-less $\text{Ba}_{1-a}\text{K}_a\text{Pb}_{1-b}\text{Bi}_b\text{O}_3$ can be reclassified as a high-temperature superconductor,⁵⁹ although discovered by Sleight, Gillson, and Bierstedt⁶⁰ long before the discovery of high-temperature superconductivity by Bednorz and Müller.⁶¹

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¹J. E. Hirsch and F. Marsiglio, *Physica C* **162–164**, 591 (1989).

²D. I. Khomskii and A. Z. Zvezdin, *Solid State Commun.* **66**, 651 (1988).

³H. A. Blackstead and J. D. Dow, *Pis'ma Zh. Eksp. Teor. Fiz.* **59**, 262 (1994) [*JETP Lett.* **59**, 283 (1994)], and references therein.

⁴See, for example, A. Millis, H. Monien, and D. Pines, *Phys. Rev. B* **42**, 167 (1990); R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993).

⁵Y. Tokura, H. Takagi, and S. Yoshida, *Nature (London)* **337**, 345 (1989).

⁶A. Manthiram and Y. T. Zhu, *Physica C* **226**, 165 (1994).

⁷H. Ishii, T. Koshizawa, T. Hanyu, and S. Yamaguchi, *Jpn. J. Appl. Phys.* **32**, 1070 (1993).

⁸C. Lin, G. Lu, Z.-X. Liu, and Y. F. Zhang, *Physica C* **194**, 66 (1992).

⁹W. J. Zhu, Y. S. Yao, X. J. Zhou, B. Yen, C. Dong, Y. Z. Huang, and Z. X. Zhao, *Physica C* **230**, 385 (1994).

¹⁰Z. X. Zhao, G. C. Che, Y. C. Lan, and A. M. Hu, *Solid State Commun.* **96**, 401 (1995).

¹¹G. Er, Y. Miyamoto, F. Kanamaru, and S. Kikkawa, *Physica C* **181**, 206 (1991).

¹²M. G. Smith, A. Manthiram, J. Zhou, J. B. Goodenough, and J. Markert, *Nature (London)* **351**, 549 (1991).

¹³S. Takano, S. I. Makamura, Y. Terashima, and T. Mikura, *Science C* **206**, 95 (1993).

¹⁴C. L. Seaman, N. Y. Ayoub, T. Björnholm, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Markert, J. J. Neumeier, P. K. Tsai, and M. B. Maple, *Physica C* **159**, 391 (1989); C. L. Seaman, N. Y. Ayoub, T. Björnholm, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Markert, J. J. Neumeier, P. K. Tsai, and M. B. Maple, *ibid.* **159**, 391 (1989); J. T. Markert, J. Beille, J. J. Neumeier, E. A. Early, C. L. Seaman, T. Moran, and M. B. Maple, *Phys. Rev. Lett.* **64**, 80 (1990).

¹⁵We emphasize how very important the observation that $\text{Tm}_{2-z}\text{Ca}_z\text{CuO}_4$ superconducts is. The superconductivity in this material and in related $R_{2-z}\text{Ca}_z\text{CuO}_4$ materials (with heavy-mass, small-radius rare-earth ions) should be thoroughly studied. This single datum currently provides the primary evidence (i) that $R_2\text{CuO}_4$ can be doped p -type with Ca and superconduct, and (ii) that interstitial oxygen is not necessary for superconductivity (but holes are). In addition, it confirms that the size of the rare-earth ion is not the single essential parameter governing superconductivity. Persons advocating n -type superconductivity in $R_{2-z}\text{Ce}_z\text{CuO}_4$ can also cite it as evidence (albeit not very strong evidence) of particle-hole symmetry. It is important that any controversy surrounding this datum be removed. Accordingly, we have indicated which of our conclusions rely on this datum, and emphasize that most of our conclusions are independent of it.

¹⁶Y. K. Tao, M. Bonvalot, Y. Y. Sun, R. L. Meng, P. H. Hor, and

- C. W. Chu, *Physica C* **165**, 13 (1990).
- ¹⁷I. Mangelschots, N. H. Andersen, B. Lebeck, A. Wisniewski, and C. S. Jacobsen, *Physica C* **203**, 369 (1992).
- ¹⁸J. E. Robinson, *Phys. Rev.* **161**, 533 (1967); J. E. Robinson and J. D. Dow, *ibid.* **171**, 815 (1968); *Phys. Rev. B* **3**, 2818 (1971).
- ¹⁹Wu Jiang, S. N. Mao, X. X. Xi, X. -G. Jiang, J. L. Peng, T. Venkatesan, C. J. Lobb, and R. L. Greene, *Physica C* **235–240**, 1403 (1994).
- ²⁰S. N. Mao, X. X. Xi, Q. Li, L. Takeuchi, S. Bhattacharya, C. Kwon, C. Doughty, A. Walkenhorst, T. Venkatesan, C. B. Whan, J. L. Peng, and R. L. Greene, *Appl. Phys. Lett.* **62**, 2425 (1993).
- ²¹H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, *Phys. Rev. Lett.* **44**, 810 (1980); J. D. Dow, in *Highlights of Condensed-Matter Theory*, Proceedings of the International School of Physics Enrico Fermi, Course 89, Varenna, 1983, edited by F. Bassani, F. Fumi, and M. P. Tosi (Societa Italiana di Fisica, Bologna, Italy, and North-Holland, Amsterdam, 1985), pp. 465–494.
- ²²C. S. Lent, M. A. Bowen, R. S. Allgaier, J. D. Dow, O. F. Sankey, and E. S. Ho, *Solid State Commun.* **61**, 83 (1987).
- ²³P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, J. L. Peng, and R. L. Greene, *Phys. Rev. B* **49**, 15 322 (1994).
- ²⁴P. Ghigna, G. Spinolo, A. Filipponi, A. V. Chadwick, and P. Hanmer, *Physica C* **246**, 345 (1995).
- ²⁵P. Ghigna, G. Spinolo, M. Scavini, U. Anselmi Tamburini, and A. V. Chadwick, *Physica C* **253**, 147 (1995).
- ²⁶Zengquan Tan, M. E. Filipkowski, J. I. Budnick, E. K. Heller, D. L. Brewster, B. L. Chamberland, C. E. Bouldin, J. C. Woicik, and D. Shi, *Phys. Rev. Lett.* **64**, 2715 (1990).
- ²⁷S. B. Qadri, M. S. Osofsky, V. M. Browning, and E. F. Skelton, *Appl. Phys. Lett.* **68**, 2729 (1996).
- ²⁸J. C. Phillips, *Physica C* **221**, 327 (1994); *Phys. Rev. B* **46**, 8542 (1992).
- ²⁹In the zero defect-host coupling limit, the interstitial oxygen is neutral and the Ce is Ce^{+3} . With nonzero coupling, the Ce can donate its electron, becoming Ce^{+4} , and the oxygen can yield up to two holes to the host, becoming O^{-2} . The oxygen must be ionized to O^{-1} or a more-negative charge state if the Ce is Ce^{+4} and the host is doped p -type.
- ³⁰R. V. Kasowski, M.-H. Tsai, and J. D. Dow, *Phys. Rev. B* **41**, 8949 (1990).
- ³¹H. A. Blackstead and J. D. Dow, *J. Appl. Phys.* **78**, 7175 (1995).
- ³²H. A. Blackstead and J. D. Dow, *J. Phys. Chem. Solids* **56**, 1697 (1995); H. A. Blackstead, J. D. Dow, J. F. Federici, W. E. Packard, and D. B. Pulling, *Physica C* **235–240**, 2161 (1994).
- ³³S. Massidda, N. Hamada, J. Yu, and A. J. Freeman, *Physica C* **157**, 571 (1989).
- ³⁴I. D. Brown and K. K. Wu, *Acta Crystallogr. B* **32**, 1957 (1976); I. D. Brown, *Structure and Bonding in Crystals*, edited by M. O'Keefe and A. Navrotsky (Academic, New York, 1980), Vol. II, pp. 1–20; For Ce^{+3} , I. D. Brown provided the value $R_{\text{Ce}}=2.120 \text{ \AA}$.
- ³⁵R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., *Physica C* **165**, 419 (1990).
- ³⁶If σ refers to a cation (anion), the sum is over the shell of anions (cations) bonded directly to it.
- ³⁷*Ionization Potentials of Atoms and Atomic Ions*, in *Chemical Rubber Company Handbook*, 74th ed., edited by D. R. Lide (Chemical Rubber, Bombay, 1993–1994), pp. 10–205.
- ³⁸These superconductors are low-density metals, but we do not include screening, which requires a different calculation for each charge density, because it does not have a major effect on our results, and because it is zero in the insulating and low-doping limits.
- ³⁹The lattice constants of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ are $a=3.94 \text{ \AA}$ and $c=12.1 \text{ \AA}$. The positions of the atoms in the unit cell are $\text{Cu}=(0, 0, 0)$ or $(0.5, 0.5, 0.5)$; cuprate-plane oxygen= $(0, 0.5, 0)$ or $(0, 0.5, 0.5)$, O_2 -layer oxygen= $(0, 0.5, 0.25)$, and $\text{Nd}=(0, 0, 0.3523)$ or $(0.5, 0.5, 0.1477)$. [See T. Kamiyama, F. Izumi, H. Takahashi, J. D. Jorgensen, B. Dabrowski, R. L. Hitterman, D. G. Hinks, H. Shaked, T. O. Mason, and M. Seabaugh, *Physica C* **229**, 377 (1994).]
- ⁴⁰We assume that the interstitial oxygen will reside approximately at the center of the cage of neighboring oxygen ions, about midway between the O_2 - and cuprate-plane layers, at $(0.5, 0.5, 0.375)$.
- ⁴¹Steric considerations alone dictate that the Ce^{+4} ion be at least 0.1 \AA closer to the interstitial oxygen than the Nd^{+3} it replaced was (because of the difference in ionic radii). The Coulomb force between the interstitial oxygen and the Ce^{+4} causes the Ce to relax even more toward the interstitial, but x-ray data (Ref. 25), indicate that this accounts for less than another 0.1 \AA . Therefore we estimate the location of the Ce to be at $(0.5, 0.5, 0.16)$.
- ⁴²We estimate that the interstitial oxygen pushes the Cu away by ~ 0.5 to $\sim 1.0 \text{ \AA}$ in order to meet steric constraints, while allowing the Cu to remain Cu^{+2} and maintaining a Cu-interstitial-oxygen bond length that approximates the sum of ionic radii.
- ⁴³E. E. Alp, S. M. Mini, M. Ramanathan, B. Dabrowski, D. R. Richards, and D. G. Hinks, *Phys. Rev. B* **40**, 2617 (1989), and references therein.
- ⁴⁴In the spirit of the present estimates, we simply linearly interpolate the radii of O^0 and O^{-2} as a function of charge: $(0.65 + 0.375 Z_I) \text{ \AA}$. The radius of O^{-2} is given by H. T. Evans, Jr., *Ionic radii in crystals*, in *Chemical Rubber Company Handbook* (Ref. 37), p. 12-8; the O^0 radius comes from *Table of Periodic Properties of the Elements* (Sargent-Welch Scientific, Skokie, Illinois, 1980).
- ⁴⁵The charge on the interstitial oxygen was determined to be $-1.16 |e|$ by the geometrical criterion that the ionic radius of O^{-Z} for $Z=Z_I$ match the radius of the sphere inscribed in the cage formed by oxygen ions from the nearby O_2 layers and cuprate planes which surround the interstitial of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. The Cu closest to the interstitial was then allowed to relax away (in the c direction) from the interstitial and out of the cage until the interstitial's bond-valence-sum charge was also $-1.16 |e|$. Not surprisingly, at this location, the Cu assumed the approximate charge state Cu^{+2} (with charge $\approx +2.22 |e|$) and also met the (hard-sphere) steric constraints imposed by the adjacent oxygen ions. The Cu relaxation, somewhat larger than 0.5 \AA , was consistent with measurements of the interstitial oxygen bond length with Cu, of 1.99 to 2.45 \AA (Ref. 25). The Ce was then also allowed to compensate for its smaller radius as Ce^{+4} than the Nd^{+3} it replaced, by relaxing in the c direction, away from Ce's adjacent cuprate plane, about 0.16 \AA , in good agreement with the experimental estimate, $\sim 0.2 \text{ \AA}$ (Ref. 25). The oxygen ions were not allowed to assume new charges, because, with the interstitial present, oxygen-oxygen bonding (which is not well-handled by the bond-valence-sum method) becomes important.
- ⁴⁶J. Fontcuberta, L. Fabrega, M. A. Crusellas, A. Rouco, M.

- Suaiddi, A. Seffar, J. L. Garcia-Molinar, B. Martinez, S. Piñol, and X. Obradors, *Physica C* **235–240**, 142 (1994).
- ⁴⁷C. Q. Jin, Y. S. Yao, B. Q. Wu, Y. F. Xu, S. C. Liu, and W. K. Wang, *Appl. Phys. Lett.* **59**, 3479 (1991).
- ⁴⁸This suggests that pressure fabrication might increase T_c for $\text{Eu}_{2-z}\text{Ce}_z\text{CuO}_4$ and cause $\text{Dy}_{2-z}\text{Ce}_z\text{CuO}_4$ (if not magnetic) to superconduct.
- ⁴⁹Since the interstitial oxygen is located, by hypothesis (Refs. 39 and 40) about midway between the cuprate planes and the O_2 layers, the distance to an oxygen ion in either plane is approximately $1/2[a^2 + (1/16)c^2]^{1/2}$. Hence the diameter of the sphere inscribed in this oxygen cage is $d_s = [a^2 + (1/16)c^2]^{1/2} - D_Z$, where D_Z is the ionic diameter of O^{-Z} [$D_Z = 2(0.65 + 0.375 Z)$ Å] and a and c are lattice constants. The approximate condition for superconductivity is $d_s > D_1$.
- ⁵⁰T. H. Meen, H. D. Yang, W. J. Huang, Y. C. Chen, W. H. Lee, J. H. Shieh, and H. C. Ku, *Physica C* **260**, 117 (1996).
- ⁵¹The small size of Y^{+3} is why Y doping of the rare-earth site in $R_{2-z}\text{Ce}_z\text{CuO}_4$ compounds suppresses superconductivity so much faster than Gd doping. See Ref. 50.
- ⁵²The ionic radii of Ca^{+2} , Ba^{+2} , Sr^{+2} , Hf^{+4} , Ce^{+4} , Th^{+4} ; La^{+3} , Ce^{+3} , Pr^{+3} , Nd^{+3} , Sm^{+3} , Eu^{+3} , Gd^{+3} ; Tb^{+3} , Dy^{+3} , Ho^{+3} , Er^{+3} , Tm^{+3} , Yb^{+3} , Lu^{+3} ; and Y^{+3} are (in Å): 0.99, 1.12, 1.34; 0.78, 0.94, 1.02; 1.14, 1.07, 1.06, 1.04, 1.00, 0.98, 0.97; 0.93, 0.92, 0.91, 0.89, 0.87, 0.86, 0.85; and 0.92, respectively. See F. S. Galasso, *Structure, Properties, and Preparation of Perovskite-Type Compounds* (Pergamon, Oxford, 1969), p. 52.
- ⁵³ $(\text{La}_{0.67}\text{Eu}_{0.33})_{2-z}\text{Ce}_z\text{CuO}_4$ (Ref. 54) and $\text{LaNd}_{1-z}\text{Ce}_z\text{CuO}_4$ superconduct (Ref. 16), but $\text{LaGd}_{1-z}\text{Ce}_z\text{CuO}_4$ does not (Ref. 16). All three of these compounds have comparable average rare-earth ionic radii, and these radii are larger than those of $R = \text{Pr}^{+3}$, Nd^{+3} , Sm^{+3} , and Eu^{+3} , all of which lead to superconductivity of $R_{2-z}\text{Ce}_z\text{CuO}_4$. (The average radius for trivalent $\text{La}_{1/2}\text{Gd}_{1/2}$ is 1.05 Å, compared with 0.98 Å for Eu.) Therefore, size alone (Ref. 50) does not explain why Gd^{+3} destroys superconductivity, particularly in $\text{LaGd}_{1-z}\text{Ce}_z\text{CuO}_4$. We propose that crystal-field splitting (Ref. 55) also plays a role, particularly in allowing $R_{2-z}\text{Ce}_z\text{CuO}_4$ to superconduct even when the ion R is magnetic and is expected to break Cooper pairs involving oxygen $2p$ holes on nearby ions. The crystal-field splitting disables the pair breaking by those magnetic ions with total orbital angular momentum $L \neq 0$. Because Gd^{+3} has total angular momentum $L = 0$ despite being magnetic ($J \neq 0$), Gd^{+3} experiences no crystal-field splitting, Gd 's pair breaking is not disabled, and Gd poisons the superconductivity, while other magnetic rare-earth ions, such as Nd^{+3} , with $L \neq 0$, do not.
- ⁵⁴M. Yoshimoto, H. Koinuma, T. Hashimoto, J. Tanaka, S. Tanabe, and F. Soga, *Physica C* **181**, 284 (1991).
- ⁵⁵O. Peña and M. Sargent, *Prog. Solid State Chem.* **19**, 165 (1989).
- ⁵⁶The small rare-earth-radius compounds $R_{2-z}\text{Ce}_z\text{CuO}_4$ apparently neither superconduct nor can be doped with significant amounts of Ce. [H. Okada, M. Takano, and Y. Takeda, *Phys. Rev. B* **42**, 6813 (1990) and private communication.] In contrast, Th-doped $\text{Eu}_{2-z}\text{Th}_z\text{CuO}_4$ does not superconduct, but apparently may dissolve Th (Ref. 14). The small rare-earth-radius alloys $(\text{Nd}_{1-y}\text{Y}_y)_{2-z}\text{Ce}_z\text{CuO}_4$ superconduct for moderately large radii ($y < 0.3$), but not for smaller radii such as that corresponding to $y = 0.3$; and the nonsuperconducting alloys, in contrast to the materials with only one kind of large ion, apparently can be doped with Ce, although it is not known if the samples have Ce inhomogeneously distributed preferentially in the Nd-rich regions. If, on the one hand, the alloy samples are truly homogeneous, then the nonsuperconducting $(\text{Nd}_{1-y}\text{Y}_y)_{2-z}\text{Ce}_z\text{CuO}_4$ and $\text{Eu}_{2-z}\text{Th}_z\text{CuO}_4$ materials provide experimental proof that the Ce-doped and Th-doped $R_2\text{CuO}_4$ systems lack particle-hole symmetry in the mechanism of superconductivity (and hence contradict most cuprate-plane models of high-temperature superconductivity). If, on the other hand, sample inhomogeneities mask the fact that Ce solubility becomes vanishingly small in localities that are Y rich, then the Ce-doping data are compatible with a lack of particle-hole symmetry in the doping, but are not necessarily inconsistent with particle-hole symmetry in the mechanism of superconductivity. In this latter case, the Ce doping and Th doping produce different results: only the Ce-doping data are also consistent with $Z = 1$ being the condition for successful Ce doping, and only $\text{Gd}_{2-z}\text{Ce}_z\text{CuO}_4$ of the $R_{2-z}\text{Ce}_z\text{CuO}_4$ compounds is Ce doped and does not superconduct—evidence that the failure of $\text{Gd}_{2-z}\text{Ce}_z\text{CuO}_4$ is singular and hence related to its lack of crystal-field splitting (rather than to ionic size). The observation of significant crystal-field splitting in $\text{Pr}_{2-z}\text{Ce}_z\text{CuO}_4$ (Ref. 14) also lends credence to the claim that the crystal-field effect is important in these materials. The situation may be different for Ca doping. For example, $\text{Dy}_{2-z}\text{Ca}_z\text{CuO}_4$ probably does not superconduct because of its antiferromagnetism (associated with ordering of its Dy^{+3} moments at 9 K) and its collective magnetic fluctuations well above 9 K,⁹ which destroy superconductivity.
- ⁵⁷H. A. Blackstead and J. D. Dow, *Philos. Mag. B* **72**, 529 (1995).
- ⁵⁸H. A. Blackstead and J. D. Dow, *Proc. SPIE* **2397**, 617 (1995); *High-temperature superconductivity*, in Proceedings of the Second International Symposium on Quantum Confinement Physics and Applications, edited by M. Cahay, S. Bandyopadhyay, J. P. Leburton, A. W. Kleinsasser, and M. A. Osman (Electrochemical Society, Pennington, NJ, 1994), Vol. 94-17, p. 408; *Superlattice model of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_x$* , *ibid.*, p. 419.
- ⁵⁹R. G. Goodrich, C. Grienier, D. Hall, A. Lacerda, E. G. Haanappel, D. Rickel, T. Northington, R. Schwarz, F. M. Mueller, D. D. Koelling, J. Vuillemin, L. Van Bockstal, M. L. Norton, and D. H. Lowndes, *J. Phys. Chem. Solids* **54**, 1251 (1993).
- ⁶⁰A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, *Solid State Commun.* **17**, 27 (1975).
- ⁶¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).