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Signatures of nearly invisible defects in $PrBa_2Cu_3O_7$ and $Pr_{2-z}Ce_zSr_2Cu_2NbO_{10}$

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Pr_{Ba} and Pr_{Sr} are the defects responsible for the suppression of superconductivity in $PrBa_2Cu_3O_7$ and in $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$, respectively, and are difficult to detect with conventional techniques. Even neutron scattering has difficulty detecting Pr_{Ba} because the scattering lengths of Pr and Ba are so similar. In this paper, we point out how these alkaline-earth-site Pr defects can be readily detected indirectly in fully oxygenated samples, using measurements of the *c*-axis lengths.

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I. INTRODUCTION

With the demonstration that $PrBa_2Cu_3O_7$ (Fig. 1) superconducts at a critical temperature of roughly 90 K,[1–12] as predicted,[1,2] it is desirable to know what the conditions are that characterize materials which superconduct. The $PrBa_2Cu_3O_7$ compounds which do superconduct are the ones with few if any Pr-on-Ba-site (Pr_{Ba}) defects,[13] but these defects are difficult to detect even directly with neutrons, since Pr and Ba have almost the same neutron-scattering lengths.[14] Furthermore, since both Pr and Ba are ions with similar high nuclear charges, x-ray scattering does not discriminate between them easily either.

In this paper, we suggest a way to determine the approximate Pr_{Ba} content in $PrBa_2Cu_3O_7$, by measuring the material's *c*-axis length with x-ray diffraction. We also argue that a high Néel temperature, the amount of $BaCuO_2$ impurity phase contained in the sample, the number of O(5) defects, and a short *c*-axis lattice constant all signal defective material that is unlikely to superconduct. These other quantities, especially the lattice constant, are easier to measure than the number of Pr_{Ba} defects, because the defects are almost invisible even to neutrons.

II. $RBa_2Cu_3O_7$

Flux-grown $PrBa_2Cu_3O_x$ (with $x \approx 7$) (Ref. 15) has a short *c*-axis lattice constant (and does not superconduct), while the same material grown by the traveling-solvent floating-zone (TSFZ) scheme[15–17] does superconduct and has a longer *c* axis—near the value predicted by extrapolating data for the other (rare-earth)$Ba_2Cu_3O_7$ compounds (see Fig. 2).[18,19] The TSFZ material has a critical temperature of 80–85 K,[15,20] slightly less than the optimal T_c,[9] indicating that it still very likely has some Pr_{Ba} defects. Indeed, the prescription for optimizing the critical temperature is both to optimize the oxygen content and to minimize the number of Pr_{Ba} defects. In this paper, we assume that, to an adequate approximation, oxygen content has been optimized. (We do know that increasing the oxygen content from $x=6$ to $x=7$ leads to contraction of the *c*-axis length.[21])

Recently, Araujo-Moreira *et al.*[12] have also reported superconducting $PrBa_2Cu_3O_7$, and their material also has a long *c* axis, near the line of Fig. 2 and in agreement with TSFZ-$PrBa_2Cu_3O_7$, which also superconducts.

$CmBa_2Cu_3O_7$,[22] which has not yet been observed to superconduct, appears to be singularly distant from the line in Fig. 2 that defines the *c*-axis lengths of the superconductors of this class, as is also the case for flux-grown (nonsuperconducting) $PrBa_2Cu_3O_7$. This suggests that ''clean'' $PrBa_2Cu_3O_7$ material[22] (i) will superconduct and (ii) will have a *c*-axis length about 0.05 Å longer than the *c* axis of

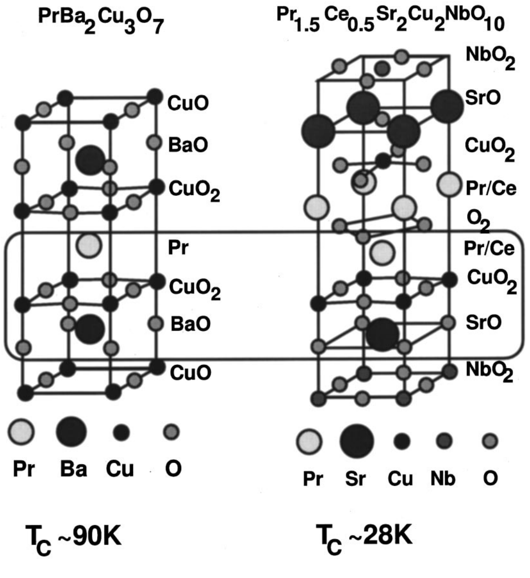

FIG. 1. Crystal structures of (a) $PrBa_2Cu_3O_7$ and (b) $Pr_{2-z}Ce_zSr_2Cu_2NbO_{10}$.

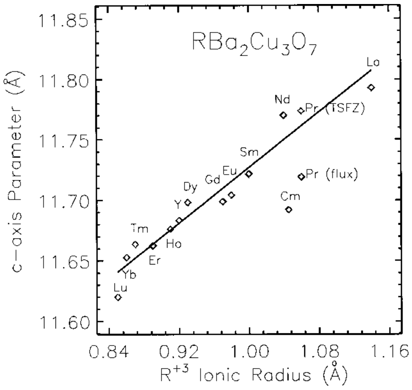

FIG. 2. The *c*-axis lattice parameter of the $R\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_7$, after Ref. 18 versus trivalent rare-earth (R) ionic radius as obtained from Ref. 19. Data for $R=\mathrm{Y}$ and Cm are also included. Two data points are plotted for Pr; the material with the longer *c* axis had the lower reported Néel temperature.

the present ‘‘dirty’’ flux-grown material. Certainly the ‘‘dirty’’ $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$ (and very likely the conventionally prepared $\mathrm{CmBa}_2\mathrm{Cu}_3\mathrm{O}_7$) materials have numerous $\mathrm{Pr}_{\mathrm{Ba}}$ (and $\mathrm{Cm}_{\mathrm{Ba}}$) defects.[23,24]

III. NÉEL TEMPERATURE

One of the interesting facts about superconducting $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$ that distinguishes it from nonsuperconducting material is that its Néel temperature is less than 5 K,[25] although the Néel temperature of non-superconducting $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$ is reported to be as high as 17 K for $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$ (Ref. 26) [and 22 K for $\mathrm{CmBa}_2\mathrm{Cu}_3\mathrm{O}_7$ (Ref. 27)]. We believe that this major reduction in the Néel temperature of superconducting $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$ samples is due to the absence of $\mathrm{Pr}_{\mathrm{Ba}}$ defects which occur in contents of order 0.10 in the nonsuperconducting homologues, as in $\mathrm{CmBa}_2\mathrm{Cu}_3\mathrm{O}_7$ (which almost certainly contains $\mathrm{Cm}_{\mathrm{Ba}}$ defects). These $\mathrm{Pr}_{\mathrm{Ba}}$ (and $\mathrm{Cm}_{\mathrm{Ba}}$) defects, in a sense, provide additional coupling between the rare-earth ions $\mathrm{Pr}_{\mathrm{Pr}}$ (and $\mathrm{Cm}_{\mathrm{Cm}}$) by reducing the average distance between them, and hence cause the Néel temperature to increase by increasing the *effective* $\mathrm{Pr}_{\mathrm{Pr}}$–$\mathrm{Pr}_{\mathrm{Pr}}$ interaction.

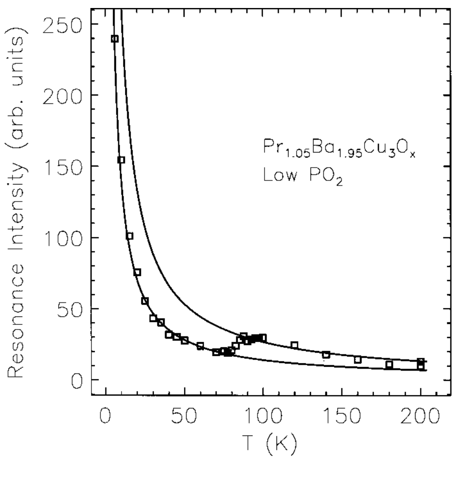

FIG. 3. Cu electron spin resonance intensity (in arbitrary units) versus temperature (in K) of $\mathrm{Pr}_{1.05}\mathrm{Ba}_{1.95}\mathrm{Cu}_3\mathrm{O}_x$ with $x\approx 7$. Note that as the temperature drops through $T\approx 92$ K the number of resonating spins decreases to about half of the number of spins above T_c. This is evidence of a mesoscopic Meissner effect.

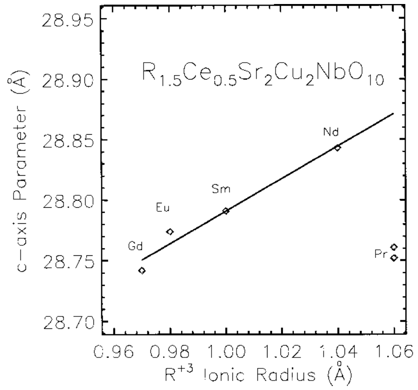

FIG. 4. The *c*-axis lattice parameter of the $R_{1.5}\mathrm{Ce}_{0.5}\mathrm{Sr}_2\mathrm{Cu}_2\mathrm{NbO}_{10}$, after Refs. 33 and 34 versus trivalent rare-earth ionic radius as obtained from Ref. 19. Two data points are plotted for Pr; the material with the longer *c* axis had the lower Néel temperature.

IV. BaCuO_2 DEFECTS

When Pr occupies Ba sites, an impurity phase of BaCuO_2 occurs,[28] because of the extra material left over. This phase can be detected by Cu electron-spin resonance in *granular* $\mathrm{Pr}_{1+u}\mathrm{Ba}_{2-u}\mathrm{Cu}_8\mathrm{O}_x$ (with $x\approx 7$) (see Ref. 4 for a discussion of sample preparation). The resonance signal varies as NT^{-1}, where T is the temperature and N is the number of resonating spins. Since some of the spins are screened in superconducting material ($T_c\approx 92$ K) by a local Meissner effect (which causes about half of the Cu spins to stop resonating), the number of resonating spins N drops [by almost a factor of 2 for the sample of Fig. 3 (Ref. 4)] when the temperature is decreased through T_c.

V. O(5) DEFECTS

To facilitate substitution of $\mathrm{Pr}_{\mathrm{Ba}}$, namely Pr^{+3} on a Ba^{+2} site, some O(5) oxygen forms.[29] In all likelihood, about one O(5) for two $\mathrm{Pr}_{\mathrm{Ba}}$ defects forms to balance charge.[30] Therefore the three defects, O(5), BaCuO_2, and $\mathrm{Pr}_{\mathrm{Ba}}$, act as signatures of the formation of imperfect $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$. Normally the imperfect material does not superconduct, because it contains too many Cooper pair-breaking defects $\mathrm{Pr}_{\mathrm{Ba}}$.

VI. LATTICE CONSTANT OF $R_{1.5}\mathrm{Ce}_{0.5}\mathrm{Sr}_2\mathrm{Cu}_2\mathrm{NbO}_{10}$

An effective way to search for $\mathrm{Pr}_{\mathrm{Ba}}$ defects in $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_7$ is via the *c*-axis lattice parameter, which is known to be anomalously short in all but the purest materials—and becomes shorter when $\mathrm{Pr}_{\mathrm{Ba}}$ is present.[31] The lattice parameter of $\mathrm{Pr}_{1.5}\mathrm{Ce}_{0.5}\mathrm{Sr}_2\mathrm{Cu}_2\mathrm{NbO}_{10}$ is also known to be anomalously short: 28.72 Å (Ref. 32) or 28.75 Å,[33,34] instead of the 28.87 Å expected by plotting the *c*-axis parameter versus the triva-

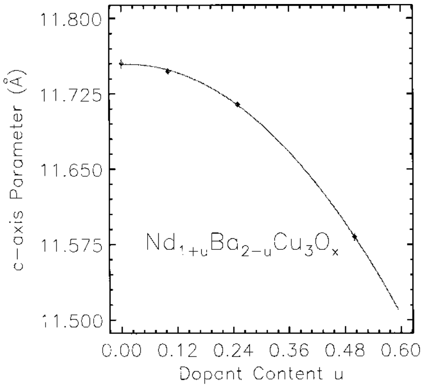

FIG. 5. The c-axis lattice parameter of $Nd_{1+u}Ba_{2-u}Cu_3O_x$ with $x \approx 7$ versus Pr_{Ba} dopant content u, based on data from Ref. 35. The data are plotted with error bars that are five times as large as they should be (to make them visible).

lent rare-earth radii for all rare-earth ions (Fig. 4). In the case of $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (Fig. 1), there is sufficient neutron contrast between Pr and Sr, so that neutrons easily determine that there are about 23%(+7%/−8%) (Ref. 30) Pr_{Sr} defects in the samples we have measured. These defects are also responsible for the short lattice constant.

The Néel temperature of $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ is apparently controversial. Felner *et al.*[32] suggest that the Pr sublattice does not order at all, while Goodwin *et al.* claim that T_N depends on the sample, having reported it to be both 10 K (Ref. 33) and 17 K (Ref. 34). This may be symptomatic of an effect due to Pr_{Sr} defects: The 10 K sample (Fig. 4) has a longer c axis than the 17 K sample, as would be expected for fewer Pr_{Sr} defects.

The authors of Ref. 33 have argued that the mechanism for the suppression of superconductivity in $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ is the same as in $PrBa_2Cu_3O_7$, and we agree. The mechanism is pair breaking by Pr_{Sr} defects in $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (or by Pr_{Ba} in $PrBa_2Cu_3O_7$). By analogy with $PrBa_2Cu_3O_7$, if the Néel temperature is indeed in the range of 10–17 K, as Goodwin *et al.* claim, we suggest that the Néel temperature of $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ should drop to about 2 K or less if the Pr_{Sr} defects are removed, in which case the material should exhibit bulk superconductivity.

VII. LATTICE CONSTANT OF $PrB_2Cu_3O_7$

Likewise, we expect a short c axis in defective $PrBa_2Cu_3O_7$, and shall assume that in perfect material

$$c(PrBa_2Cu_3O_7) = c(NdBa_2Cu_3O_7) + \Delta c,$$

where we have $\Delta c = 0.0115$ Å, the difference in the c-lattice constants of $PrBa_2Cu_3O_7$ and $NdBa_2Cu_3O_7$ obtained from the line of Fig. 2.

Consequently we can obtain for $Pr_{1+u}Ba_{2-u}Cu_3O_7$ a c-axis length as a function of Pr_{Ba} defect content u. Using the fit to the c-axis lattice constants of the $RBa_2Cu_3O_7$ compounds (the straight line in Fig. 2), and the dependence on $(\text{rare-earth})_{Ba}$ antisite defect dopant concentration u found by Kramer *et al.* (Fig. 5),[35] we obtain the approximate expression for the (properly oxygenated) c-axis parameter of $Pr_{1+u}Ba_{2-u}Cu_3O_x$ compounds (where $x \approx 7$) to be

$$c(Pr_{1+u}Ba_{2-u}Cu_3O_x) = \Delta c + D - Eu - Fu^2,$$

where we have $D = 11.754$ Å, $E = 0.017\,439$ Å, and $F = 0.721\,18$ Å.

One thing is clear: the researchers[7,12] who have fabricated $PrBa_2Cu_3O_7$ with a c axis longer than 11.76 Å have also observed bulk superconductivity, while those who have found $c < 11.72$ Å have not observed superconductivity.[36–38] Clearly the nonsuperconducting materials have short c axes and hence about $u > 0.23$ undetected pair-breaking Pr_{Ba} defects—more than enough to destroy the superconductivity. Ba_{Pr} defects cannot explain the changes in the c-axis length because Ba does not dissolve on rare-earth sites in $(\text{rare-earth})Ba_2Cu_3O_7$ compounds.[39]

Moreover, it is well known that La easily occupies Ba sites in $LaBa_2Cu_3O_7$, and several researchers have recently shown that there are indeed numerous Pr_{Ba} defects in conventionally prepared $PrBa_2Cu_3O_7$ material.[40,41] Not only does $NdBa_2Cu_3O_7$ have some Nd_{Ba} defects,[42] but the Ba site of $PrBa_2Cu_3O_7$ also has some Pr defects, as noted first by Nutley *et al.*[43] and more recently by Shukla *et al.*[11] The solubility of Pr_{Ba} defects should be between the solubilities of La_{Ba} in $LaBa_2Cu_3O_7$ and Nd_{Ba} in $NdBa_2Cu_3O_7$.

VIII. CONCLUSION

The approximate formula above for the c-axis length can be used to estimate the concentration u of antisite Pr_{Ba} defects, and to infer the quality of $PrBa_2Cu_3O_7$ samples—so that improved sample-preparation procedures can be readily developed. That way, one can determine if the $PrBa_2Cu_3O_7$ is sufficiently defect-free that it is likely to superconduct—or nearly superconduct.

Furthermore, measurements of the $BaCuO_2$ and the O(5) defect concentrations should confirm the general conclusions drawn from the c-lattice constants, and should facilitate the development of ''clean'' superconducting $PrBa_2Cu_3O_7$.

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