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Isotope effect in high-T_c superconductors

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For high-T_c superconductors in which transition temperatures T_c are reduced by doping, the oxygen isotope effect (OIE) coefficient in T_c is shown to increase systematically with the pair-breaking rate and with the valence difference between the substituted and native ions. Moreover, the OIE in T_c tends to zero as one approaches optimum (or ideal) stoichiometry at which the quality of the superconducting condensate is maximized. In materials with *isovalent* substitutions, e.g., Sr for Ba or Zn for Cu in $YBa_2Cu_3O_{7-\delta}$, the small OIE of the parent (unsubstituted) compound is magnified owing to pair-breaking disorder. In materials with *heterovalent* substitutions, e.g., La or Pr for Ba, where carrier densities are necessarily changed, pair breaking induces a much larger OIE. A seminal case is Pr-doped $YBa_2Cu_3O_{7-\delta}$, where data were previously misinterpreted owing to the false assumption that Pr substitutes only for Y. It is now clear, however, that the decrease in T_c observed with Pr doping actually arises from pair breaking caused by Pr-on-Ba-site defects introduced during crystal growth. When $PrBa_2Cu_3O_{7-\delta}$ is grown correctly without such defects, T_c remains unchanged (as in the case of most other rare-earth substitutions for Y). Invariance of T_c under a 60% rare-earth mass increase provides strong evidence against phononic pairing mechanisms. The fact that T_c drops when Pr substitutes for Ba but not for Y indicates that the superconducting hole condensate resides in the BaO layers, where pair breaking degrades T_c and dramatically increases the OIE. Superconductive pairing modeled on Coulomb coupling between the hole (BaO) and the electron (CuO_2) layers is shown to resolve the serious shortcomings inherent in approaches based on electron-phonon interactions and is found to be generally applicable. Moreover, the OIE in the magnetic penetration depth in alloys is shown to be constant, with degradation of T_c up to 50%, and thus is unrelated to the OIE in T_c.

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I. INTRODUCTION

Unlike conventional phonon-mediated superconductors, high-T_c materials are characterized by carriers that are necessarily confined to two dimensions.[1] In these materials, doping often introduces pair-breaking effects, thus compromising the quality of the superconducting condensate (characterized, e.g., by a suppression of T_c, a reduced Meissner fraction, and a broadening of the transition width ΔT_c). A unique set of features was also shown to exist characterizing "optimized" high-T_c superconductivity, in which disorder-induced pair-breaking effects vanish. Included in these features is a vanishingly small isotope effect (as one approaches optimum stoichiometry), much smaller that that observed for phonon-mediated superconductors.[2,3]

Early studies of the oxygen isotope effect (OIE) in T_c for $^{16}O \rightarrow {}^{18}O$ substitution performed on optimized polycrystalline $YBa_2Cu_3O_{7-\delta}$ (Hoen *et al.*[4]), where nearly complete oxygen exchange has been obtained, found an isotopic mass effect for O isotope substitution, $T_c \sim M^{-\alpha_O}$, with $\alpha_O \leqslant 0.03$ where M is the O mass. The measured OIE coefficient is thus too small for phonon-mediated superconductive pairing (e.g., $\alpha_O = 0.5$ in the case of BCS theory[5]).

Moreover, it was pointed out by Hoen *et al.*[4] that substitution of Y by large rare-earth elements with large mass differences has virtually no effect on T_c. Mass changes at the Y site were 60% or more, nearly five times greater than those at the O sites. The fact that T_c is virtually independent of rare-earth substitution at the Y site provides strong experimental justification for ruling out phononic (or polaronic[6]) mechanisms of high-T_c superconductivity, including nonadiabatic electron-phonon interactions (involving e.g., Jahn-Teller and proximity effects). It also agrees with the conclusion that conventional electron-phonon interactions are too weak to explain the high transition temperatures.[7,8]

While studies of the OIE have also included nonoptimum alloyed samples (exhibiting significant pair breaking),[9–13] certain experimenters have warned about making phonon-based interpretations of OIE data for alloyed samples in which T_c is depressed, noting correlations among the OIE coefficient, the width of the superconducting transition, and an incomplete Meissner fraction.[9] Indeed, it was first shown by Kresin *et al.* that both a depressed T_c and an enhanced OIE in T_c in certain alloys could be explained with a spin-flip pair-breaking model.[14] While pair breaking turns out to be central to explaining the OIE in high-T_c materials, the model presented (Ref. 14) is inconsistent with experiment, as discussed below. These and other authors have treated the OIE in the context of nonadiabatic electron-phonon interactions[15–18] and polarons.[10–13] In contrast, we show that pair breaking, when generalized to include nonmagnetic disorder and superconductive pairing via Coulomb interactions, provides an excellent account of the data for the depressed T_c, the enhanced OIE in the nonoptimum alloys, and the small OIE in the best optimized samples.

A case study of the OIE in Pr-doped $YBa_2Cu_3O_{7-\delta}$ is emphasized in this paper because, when correctly interpreted, experiment unambiguously shows that high-T_c superconductivity involves the presence of mobile charge carriers in both the CuO_2 and BaO layers, i.e., not just in the cuprate layers. While Pr-doped $YBa_2Cu_3O_{7-\delta}$ was found in the early days of high T_c to be nonsuperconducting,[19,20] it was subsequently predicted[21] and measurements unambiguously determined[22–25] that Pr-on-Ba-site defects (and not Pr substituting for Y) were responsible for the suppressed T_c. By using proper growth techniques, the Pr-on-Ba-site defects were eliminated, yielding a $T_c \sim 90$ K and a full Meissner fraction.

Materials of the (rare earth)$Ba_2Cu_3O_{7-\delta}$ type all form single-phase compounds for Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu on the rare-earth site (i.e., between the CuO_2 planes), with superconducting transition temperatures of order of 90 K. Only Tb-, Ce-, and Pr-substituted materials were originally found to be nonsuperconducting.[26] Partial Tb substitution in $(Y_{1-x}Tb_x)Ba_2Cu_3O_{7-\delta}$ (for $x < 0.5$) produces a superconductor without degradation of T_c (~ 90 K). The Ce-doped material, on the other hand, appears to produce Ce in the Ce^{+4} valence state, whereas the other rare earths have a +3 valence in (rare earth)$Ba_2Cu_3O_{7-\delta}$. The nonsuperconductivity of $PrBa_2Cu_3O_{7-\delta}$ was eventually correlated with the fact that its *c* axis was significantly shorter than expected for a rare-earth ion of radius of 1.13 Å, the value appropriate to Pr^{+3}. The short *c* axis was attributed to the presence of Pr-on-Ba-site defects, which also caused pair breaking.[21]

In 1997, Zou *et al.*[22] finally synthesized bulk superconducting $PrBa_2Cu_3O_{7-\delta}$ using a traveling-solvent floating-zone method, producing a crystal with zero resistance at $T_c = 80$ K, and fully superconducting according to its measured Meissner fraction. The material was improved in 1999 to yield a T_c of 90 K.[23] Later, Cu nuclear quadrupole resonance measurements confirmed the presence of Pr-on-Ba-site defects in nonsuperconducting $PrBa_2Cu_3O_{7-\delta}$.[25,26] Since Pr-on-Ba-site defects are located in the BaO layer, their destructive effect on the superconductivity implies that the bands associated with the BaO layers are important for superconductivity. Given the added fact that the pairing symmetry is nodeless and presents no Cu *d*-band signature,[27,28] it is not plausible to claim that the superconducting hole condensate for $PrBa_2Cu_3O_{7-\delta}$ and other (rare earth)$Ba_2Cu_3O_{7-\delta}$ compounds is located in the cuprate planes.[29,30]

Despite the above evidence, Keller and co-workers, relying heavily on Pr-doped $YBa_2Cu_3O_{7-\delta}$ samples with depressed T_c and obviously containing a high density of Pr-on-Ba-site defects, conducted their studies of the OIE.[10–13] They assumed that $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$, was being studied, whereas the actual composition should be written as $(Y_{1-x+y}Pr_xBa_{2-y})Cu_3O_{7-\delta}$, where the quantity *y* denotes the fraction of Pr-on-Ba-site defects. Hence, many of the superconducting transition temperatures reported for $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ actually correspond to measurements of $(Y_{1-x+y}Pr_xBa_{2-y})Cu_3O_{7-\delta}$, with Pr-on-Ba-site defects [we postulate that the OIE in actual $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ does not change significantly with Pr doping, since T_c is essentially unchanged]. This misrepresentation led to several erroneous conclusions, most notably attributing the OIE observed for the CuO_2 layer oxygens to polaron-mediated superconductivity in the CuO_2 planes. In this work, we show that a pair-breaking model with superconductivity comprising carriers in BaO and CuO_2 layers can account for the observed trends in the OIE data.

High-T_c superconductors also exhibit an OIE in the magnetic penetration depth,[10,31] in which theory for conventional superconductors predicts a negligible OIE. The OIE has been studied in both optimum and substituted compounds and has stimulated various theoretical investigations that consider this phenomenon in terms of nonadiabatic electron-phonon interactions.[15–19] In the London model, the *ab*-plane penetration depth (i.e., the penetration depth measured in the *ab* plane) at zero temperature is expressed in terms of the *ab* basal plane effective mass m_{ab}^* and the three-dimensional density n_s of the superconductive holes: $\lambda_{ab}^2(T=0) = m_{ab}^* c^2/(4\pi n_s e^2)$. Theoretical studies of the OIE in λ_{ab} have predicted that it arises from an OIE in the carrier concentration[15] or an OIE in the effective mass.[16–19] Experimental studies of the OIE in λ_{ab} at low temperature and near T_c have deduced that the OIE in m_{ab}^* is the dominant contribution.[10] However, the model that was used for separating the OIE contributions of m_{ab}^* and n_s using $\lambda_{ab}^2(T)$ near T_c could be subject to unknown systematic error, owing to the OIE in T_c.[15] A general characteristic of the OIE in the penetration depth λ_{ab} is that it reflects the OIE in normal state properties, e.g., in the carrier concentration, effective mass, or both, and is not a superconducting property *per se*. One therefore might expect there to be an OIE in the normal state *ab* plane resistivity, since it scales with $\lambda_{ab}^2(0)$ and a scattering rate. Although resistance transitions have been widely studied to determine OIE changes in T_c, differences in absolute resistivity have not been reported, possibly because experimental uncertainties in reproducing sample dimensions and probe placement could be too large.

In Sec. II of this paper, the experimental data for the OIE in $YBa_2Cu_3O_{7-\delta}$ doped with Zn^{+2}, Pr^{+3}, and La^{+3} and $La_{2-x}Sr_xCuO_4$ are discussed. Section III presents a theoretical treatment in terms of pair breaking. Section IV discusses the implications of our findings, and conclusions are given in Sec. V.

II. EXPERIMENTAL TRENDS

In Fig. 1, we have reproduced data for the OIE in T_c for Pr-doped $YBa_2Cu_3O_{7-\delta}$ (Refs. 9, 10, and 19) [correctly labeled as $(Y_{1-x+y}Pr_xBa_{2-y})Cu_3O_{7-\delta}$], La-doped $YBa_2Cu_3O_{7-\delta}$ (on Ba sites),[10,32] Zn-doped $YBa_2Cu_3O_{7-\delta}$ (on Cu sites),[9,14] and Sr-doped $YBa_2Cu_3O_{7-\delta}$ (on Ba sites).[32] Here, α_O is the T_c isotope effect exponent, T_{c0} is the maximum T_c achieved at optimal or ideal stoichiometry, and the solid and dashed

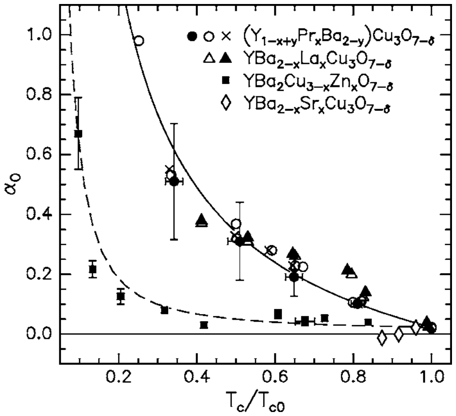

FIG. 1. Variation of oxygen isotope effect parameter with normalized transition temperatures for Pr-doped $YBa_2Cu_3O_{7-\delta}$ (Refs. 9, 10, and 19) (correctly labeled), La-doped $YBa_2Cu_3O_{7-\delta}$ (Refs. 10 and 32), Zn-doped $YBa_2Cu_3O_{7-\delta}$ (Refs. 9 and 14), and Sr-doped $YBa_2Cu_3O_{7-\delta}$ (Ref. 32). The dashed curve is the isovalent pair-breaking theory of Eq. (7a), applicable for Zn and Sr substitutions. The solid curve is the heterovalent theory of Eq. (7b), applicable for La and Pr substitutions.

curves represent the pair-breaking function described in Sec. III. A significant feature of the data in Fig. 1 is the special case of the optimum compound, $YBa_2Cu_3O_{7-\delta}$ (δ=0.05), where a very small oxygen isotope exponent, $\alpha_O \approx 0.02$, is observed, a value that is substantially smaller than the BCS expectation, $\alpha_O = 0.5$,[5] and near zero.

While data on the optimum compound, $La_{1.837}Sr_{0.163}CuO_4$,[33] are not available, extrapolation of the OIE data for $La_{2-x}Sr_xCuO_4$ in Fig. 6(b) of Ref. 9 to $x = 0.163$ suggests a small value of the exponent, $\alpha_O \ll 0.1$, at optimum stoichiometry. This is also consistent with the minimum $\alpha_O = 0.06 \pm 0.03$ found in other experiments on $La_{2-x}Sr_xCuO_4$ with $x = 0.188$.[34] The OIE results for $La_{2-x}Sr_xCuO_4$ show a widely varying dependence on x, indicating to us that pair-breaking disorder affects all studied compounds based on $La_{2-x}Sr_xCuO_4$, including the $x = 0.15$ material, which Keller[10] mistakenly associated with the T_{c0} for this series (the correct T_{c0} occurs for $x = 0.163$).

A. Isovalent versus heterovalent impurity substitution

An important feature that can be deduced from Fig. 1 concerns the valence of substitutional dopants. For example, Zn^{+2} substituting for Cu^{+2} induces a depression in T_c but a comparatively small OIE. In contrast, Pr^{+3} and La^{+3} substituting for Ba^{+2} results in a similar depression of T_c but with a significant enhancement in the OIE. Yet, the substitution of Sr^{+2} for Ba^{+2} causes only small shifts in both T_c and the OIE.[32] From these observations, one concludes that (1) the trend is that α_O tends toward zero as one approaches optimal or ideal stoichiometry, (2) T_c is depressed in substitutionally doped compounds owing to pair breaking; (3) the OIE is strongly associated with pair breaking, and (4) the site and valence of the substitutional dopant affect the magnitude and T_c dependence of the OIE.

Based on the experimental evidence (Fig. 1), we have identified two different types of impurity substitutions, corresponding to isovalent and heterovalent substitutions:

1. Isovalent impurity substitution

Although isovalent Sr substitution for Ba in $YBa_2Cu_3O_{7-\delta}$ leaves the hole concentration nominally unchanged, the Sr impurity still causes some scattering of the holes but leaves the electrons in the CuO_2 layers largely unaffected. This results in weak pair breaking, producing a modest reduction in T_c, e.g., by 13% for 50% Sr substitution for Ba (see Fig. 1). The OIE remains small,[32] however, because the hole and electron densities remain near optimal values (differences in the ionization potentials of Sr and Ba would produce small changes in the densities of mobile carriers and would only slightly affect the OIE). Similarly, substitution of Zn for Cu in $YBa_2Cu_3O_{7-\delta}$ causes scattering of electrons in the CuO_2 layers, which decreases the strength of the hole pairing and suppresses T_c. While the valence is roughly conserved, the ionic symmetries of Cu and Zn are markedly different (i.e., for Cu to have a valence of +2, it must give up a d electron; for Zn to have the same valence, it gives up its two s electrons). In this case, the OIE in Zn-substituted $YBa_2Cu_3O_{7-\delta}$ is observed to follow the standard pair-breaking formula, as first noted by Kresin *et al.*,[14] except that magnetic impurity scattering need not be invoked in the explanation.

2. Heterovalent impurity substitution

Substitution of La^{+3} for Ba^{+2} results in a valency increase of approximately +1, which acts to increase the number of electrons and thus reduce the density of holes in the BaO layer. The change in the hole density leads to a significant pair-breaking reduction in T_c (see Fig. 1). This type of impurity substitution not only suppresses T_c but also leads to an OIE that is much larger than in cases where the densities of holes (and electrons) remain unchanged (e.g., Sr substitution for Ba; Zn substitution for Cu). The effect of Pr doping has a similar effect on both T_c and the OIE because a significant fraction (y) of Pr^{+3} substitutes for Ba^{+2}.

B. Site-specific oxygen isotope effect measurements

Owing to our new understanding of Pr-doped $YBa_2Cu_3O_{7-\delta}$ (regarding the effect of Pr-on-Ba-site defects), the site-specific OIE measurements, reported in Fig. 11 of Ref. 10, require reinterpretation. We have reproduced these results in Fig. 2. The open triangles correspond to the OIE for $^{16}O \rightarrow {}^{18}O$ exchange at the CuO_2 planar (p) oxygen sites, the filled squares are the OIE measurements for the apical (BaO) and chain (CuO) oxygens, denoted as (ac) oxygens, and the open circles reflect the total ($t = p + ac$) OIE. By assuming incorrectly that Pr was substituting on only the Y sites, Keller and co-workers (see e.g., Ref. 10) drew two erroneous conclusions from these data. First, they concluded that the superconductivity was located in the CuO_2 planes (presumably, they thought that the magnetic Pr ion at the Y site acted to break pairs in the CuO_2 planes, even though similar substitutions of other rare-earth magnetic ions do not

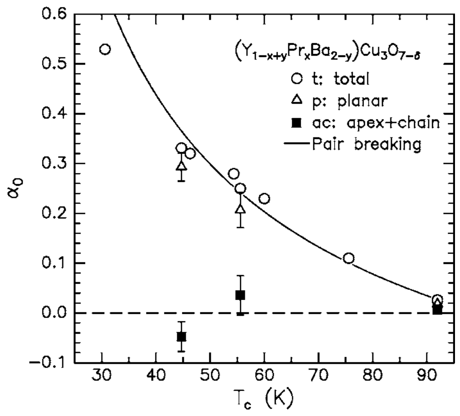

FIG. 2. Total (t) and partial (p, ac) oxygen isotope exponent α_O as a function of T_c for $(Y_{1-x+y}Pr_xBa_{2-y})Cu_3O_{7-\delta}$, where p corresponds to the cuprate-plane oxygen sites, ac corresponds to the apical and chain oxygen sites, and t $(=p+ac)$ represents all oxygen sites (after Ref. 10). The dashed line corresponds to zero. The solid curve corresponds to the heterovalent pair-breaking theory of Eq. (7b).

affect the superconductivity). Then, since the planar oxygens (open triangles) showed a dramatic OIE with decreasing T_c while the apical and chain oxygens (filled squares) show no measurable OIE, these authors then claimed erroneously that the superconducting mechanism was associated with phonon effects, specifically, small polarons.

Applying this same logic to the correct premise, namely, that T_c is depressed due to Pr-on-Ba-site defects, leads one to necessarily conclude that the pair breaking actually occurs because of a change in the BaO layers and not in the CuO_2 planes. This implies that the superconducting hole condensate resides in the BaO layers. The absence of any OIE associated with the apical (BaO) or nearby chain (CuO) oxygens thus shows that *the pairing mechanism does not depend on oxygen mass*. This means that the pairing mechanism cannot be associated with polarons or any other phonon effects which depend on the ionic mass. Moreover, the data shown in Fig. 2, when correctly interpreted, unambiguously show that the carriers in the BaO layers interact with those in the CuO_2 planes, consistent with Coulomb coupling.[1,4,7,8]

C. Oxygen isotope effect in the magnetic penetration depth

Experimental OIE data for the fractional changes in penetration depth, $\delta\lambda_{ab}/\lambda_{ab}$, and transition temperature, $\delta T_c/T_c$, for $YBa_2Cu_3O_{7-\delta}$, $(Y_{1-x+y}Pr_xBa_{2-y})Cu_3O_{7-\delta}$, and $La_{2-x}Sr_xCuO_4$ are reproduced in Fig. 3.[10] A horizontal line is drawn in Fig. 3 to illustrate that $\delta\lambda_{ab}/\lambda_{ab}$ is constant at $2.67\% \pm 0.24\%$ over a range of $\delta T_c/T_c$ from 0.2% to 3%, where T_c is depressed by almost a factor of 2 owing to pair breaking. The dashed line in Fig. 3 sketches the upward deviations that are found for samples with more strongly depressed T_c. Sample quality is greatly degraded for large depressions in T_c (as manifested by broadened superconducting transitions). The enhanced OIE in the penetration depth for $\delta T_c/T_c \sim 3\%$ thus corresponds to materials where the superconducting properties are grossly inhomogeneous. If one therefore focuses on the region $\delta T_c/T_c < 3\%$ and $T_c > \frac{1}{2}T_{c0}$, where superconducting transitions are more clearly defined, experiment shows that $\delta\lambda_{ab}/\lambda_{ab}$ is independent of T_c/T_{c0} and a constant. Here, the OIE in the magnetic penetration depth is found to be $\alpha_{O,\lambda} = 0.23 \pm 0.02$. Although the decrease in T_c in this material upon Pr doping is due to Pr-on-Ba-site defects, the OIE in λ_{ab} is observed to depend neither on T_c nor on the OIE in T_c.

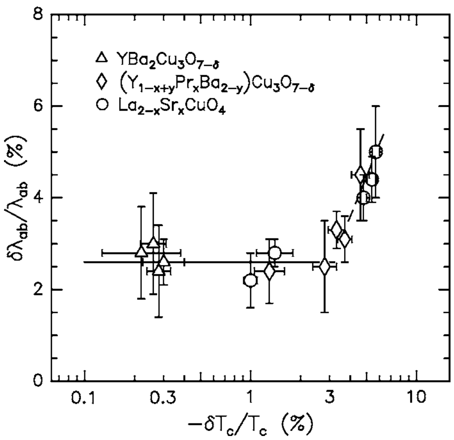

FIG. 3. The OIE shift $\delta\lambda_{ab}(0)/\lambda_{ab}(0)$ plotted against the OIE shift $-\delta T_c/T_c$ for $La_{2-x}Sr_xCuO_4$ and $(Y_{1-x+y}Pr_xBa_{2-y})Cu_3O_{7-\delta}$. The data are from various experiments and samples (the data are taken from Table 1 of Ref. 10). The horizontal solid line represents the constancy of $\delta\lambda_{ab}(0)/\lambda_{ab}(0)$ for most of the data points; the dashed line indicates the deviation for the most strongly disordered samples.

III. THEORETICAL FRAMEWORK

The disorder exhibited in $YBa_2Cu_3O_{7-\delta}$ with the various impurity substitutions results in a depression of T_c caused by pair breaking.[14] In our approach, all of the data presented in Fig. 1 are completely explained using a simple self-consistent pair-breaking model with a scattering-induced enhancement arising from a change in carrier density.

Pair breaking and the OIE in $YBa_2Cu_3O_{7-\delta}$-based superconductors are readily explained in terms of the pairing of holes in the BaO layers that is mediated by Coulomb interactions with the carriers in the CuO_2 layers. Bond valence sum (BVS) analyses, as well as consideration of charge conservation, indicate that the carriers in the CuO_2 layer are electrons.[35] The scattering of electrons by phonons associated with oxygen vibrations within the CuO_2 layers acts to reduce the net pairing attraction between holes in the BaO layers. Doping $YBa_2Cu_3O_{7-\delta}$ with Sr, Zn, La, and Pr impurities has specific effects that can be explained by superconducting pairing which is governed by hole-electron interactions, the influence of electron-oxygen-phonon scattering, and pair breaking that suppresses T_c.

A. Pair-breaking model with scattering rate enhancement

Let us assume T_{c0} to be the theoretical transition temperature in the absence of pair breaking and T_c as the transition temperature in the presence of pair breaking, characterized by a pair-breaking parameter, $\tilde{\alpha}$. The variation of T_c with pair-breaking scattering is determined by the universal relation that has been applied to both gapless superconductors[36] and disordered superconductors.[37] The general expression is given by[14]

$$\ln(T_{c0}/T_c) = \psi\left(\tfrac{1}{2} + \tilde{\alpha}/2\pi k_B T_c\right) - \psi\left(\tfrac{1}{2}\right), \tag{1}$$

where ψ is the digamma function.[38] Since nonmagnetic pair-breaking disorder in superconductors also depresses T_c,[39] it is necessary to relax the requirement of magnetic impurities given in Ref. 14. The solution of Eq. (1) for the transition temperature can be written as

$$T_c/T_{c0} = F(\tilde{\alpha}/k_B T_{c0}). \tag{2}$$

Here, the function F defines the implicit solution of Eq. (1) in terms of the reduced transition temperature. Equation (2), which determines the decrease in T_c with increasing $\tilde{\alpha}$, is plotted in Fig. 8-1 of Ref. 36.

1. *Isovalent impurity substitution*

The OIE observed in *optimal compounds* ($T_c = T_{c0}$) appears as a small shift in the transition temperature, denoted as δT_{c0} (i.e., the difference between the T_{c0} of the O^{18} sample and that of the O^{16} sample). The contribution to the OIE in *nonoptimal doped compounds* that originates from the OIE in the optimal compounds is defined as $\delta T_c^{(1)}$. A theoretical expression for $\delta T_c^{(1)}$ is derived by taking the differential of Eq. (2) with respect to T_{c0}:

$$\delta T_c^{(1)} = \delta T_{c0}[T_c/T_{c0} - (\tilde{\alpha}/k_B T_{c0})F']. \tag{3}$$

Here, $\tilde{\alpha}/k_B T_{c0} = F^{-1}(T_c/T_{c0})$ is the inverse function of F, which has the limit $F^{-1}(1)=0$; F' is the derivative of F with respect to its argument, which has the limit $F'(0) = -\pi/4$. The resulting $\delta T_c^{(1)}$ in Eq. (3) explains the OIE in T_c for compounds where cation substitution leads to pair breaking that reduces T_c without any changes in the densities of holes and electrons; examples are Zn substitution for cuprate-plane Cu or Sr substitution for Ba in $YBa_2Cu_3O_{7-\delta}$. In these cases, we have the following for the OIE parameter:

$$\alpha_O^{(1)} = -(\delta T_c^{(1)}/T_c)/(\delta M_O/M_O), \tag{4}$$

where $\delta M_O/M_O = 2/17$ for $O^{16} \rightarrow O^{18}$ isotopic substitution.

2. *Heterovalent impurity substitution*

To explain the data for the heterovalent substitutions (e.g., La and Pr substitution for Ba in $YBa_2Cu_3O_{7-\delta}$), we propose a reformulation of the result in Ref. 14, which introduced an *additional contribution* to the OIE that scales with $(n/T_c)\partial T_c/\partial n$, where n is the carrier density. A shortcoming of this approach[14] is that it predicts a change in sign and a divergent slope at $T_c = T_{c0}$ in disagreement with experiment, as noted previously.[40] Since we now know that the depression in T_c is caused by pair breaking and is not a titration (carrier density) effect, we propose to replace n by the pair-breaking parameter $\tilde{\alpha}$. This leads to an additional component to the shift in T_c of the form $\delta T_c^{(2)} \propto \tilde{\alpha}\partial T_c/\partial\tilde{\alpha}$. We approximate this by a constant scaling of the shift in T_c with pair-breaking rate, written as

$$\delta T_c^{(2)} = \gamma\tilde{\alpha}/k_B, \tag{5}$$

where γ is taken to be an empirical scaling parameter that is determined by fitting the OIE data. The form of Eq. (5) presents an additional contribution to the OIE in T_c that scales with the pair-breaking rate, $\tau^{-1} = 2\hbar^{-1}\tilde{\alpha}$.[37] This picture is therefore consistent with electron-phonon scattering that scales with the pair-breaking rate. The OIE of Eq. (5) thus yields an additional contribution to the OIE parameter given by

$$\alpha_O^{(2)} = -(\delta T_c^{(2)}/T_c)/(\delta M_O/M_O). \tag{6}$$

For the case of Sr doping (isovalent with respect to Ba^{+2}) and Zn doping (isovalent with respect to Cu^{+2}), the OIE parameter is given by

$$\alpha_O^{\mathrm{iso}} = \alpha_O^{(1)}. \tag{7a}$$

For the cases of La and Pr dopings (heterovalent with respect to Ba), the OIE parameter, derived by adding Eqs. (4) and (6), is given by

$$\alpha_O^{\mathrm{het}} = \alpha_O^{(1)} + \alpha_O^{(2)}. \tag{7b}$$

An OIE appears when disorder is sufficiently strong to induce a suppression of T_c below T_{c0}. The dashed curve in Fig. 1 is the isovalent function, $\alpha_O = \alpha_O^{(1)}$, obtained by fitting the experimental value α_O (=0.023) for $YBa_2Cu_3O_{7-\delta}$ in the limit of $\tilde{\alpha}=0$ (i.e., zero pair breaking). The theory for isovalent substitution thus provides a remarkably good fit to the observed results for Zn doping (Fig. 1). It also accounts for the small change in α_O for Sr substitution. The solid curve in Fig. 1 is a fit of the function given in Eq. (7b) for the heterovalent case, with the result $\gamma = 0.254 \pm 0.009$ for the empirical scaling parameter of Eq. (5). It is clear that the heterovalent model, which contains an enhanced OIE component that scales with the pair-breaking rate, provides an excellent fit of the OIE parameter for heterovalent substitution, i.e., when the valence is not conserved by the substitution. Our approach, with the correct identification of the Pr sites, also uses fewer fitting parameters (α_O and γ) than theory based on the (incorrect) assignment of Pr substituting only for Y.[14]

B. Oxygen isotope effect in the magnetic penetration depth

We now consider the observed T_c independence of the magnetic penetration depth OIE coefficient, $\alpha_{O,\lambda}$. The maximum transition temperature T_{c0} (corresponding to optimal superconductivity) for the high-T_c materials is a function of the two-dimensional Fermi energy ($\propto n_{2D}/m_{ab}^*$),[1] where n_{2D} is the two-dimensional hole carrier density (=n_s multiplied by the average superconducting layer spacing). Consequently, neither T_{c0} nor T_c scales linearly with the inverse square of the basal-plane penetration depth, $\lambda_{ab}^{-2}(T=0)$. This fact was recently corroborated.[39] Furthermore, the values of T_c and λ_{ab} measured in the off-stoichiometric regime, rather than correspond to intrinsic properties (such as carrier density and effective mass), reflect instead a deteriorating quality of the superconducting condensate as evidenced by the corresponding drop in Meissner fraction.

Apparent increases in the magnetic penetration depth for nonoptimal compounds can be expressed in terms of a correction factor that is analogous to the effects of scattering by impurities and crystalline disorder, in which λ_{ab}^2 is increased by a factor $1+\xi_0/1$. Here, ξ_0 is the Pippard coherence length and l is the mean free path.[36] Using the BCS model, $\xi_0 = 0.18\hbar v_F/k_B T_c$, and $l = v_F \tau$ with v_F the Fermi velocity, and identifying the scattering rate with pair breaking, $\tau^{-1} = 2\hbar^{-1}\tilde{\alpha}$,[37] one obtains λ_{ab}^2 as an implicit function of T_c,

$$\lambda_{ab}^2(T_c) = \lambda_{ab}^2(T_{c0})[1 + \eta\tilde{\alpha}/k_B T_{c0}]. \tag{8}$$

where $\eta = 2 \times 0.18$.

The results for λ_{ab} from Eq. (8) and for T_c from Eq. (2) therefore provide a consistent explanation of experimental findings: λ_{ab}^{-2} and T_c both increase monotonically on approaching the optimum limit ($\tilde{\alpha}=0$ and $T_c = T_{c0}$) and, moreover, λ_{ab}^{-2} is a nonlinear function of T_c.

The fractional OIE in the penetration depth can be derived from the differential of Eq. (8) and is given by

$$\delta\lambda_{ab}(T_c)/\lambda_{ab}(T_c) = \delta\lambda_{ab}(T_{c0})/\lambda_{ab}(T_{c0}) + \tfrac{1}{2}\eta\delta\tilde{\alpha}/k_B T_{c0}[1 + \eta\tilde{\alpha}/k_B T_{c0}]^{-1}. \tag{9}$$

The first term in Eq. (9) is the OIE in the optimum compound, whereas the second term is a correction arising from the OIE in the pair-breaking parameter, which is expressed in terms of the OIE in the transition temperature as

$$\delta\tilde{\alpha} = (\partial\tilde{\alpha}/\partial T_c)\delta T_c. \tag{10}$$

Estimates of the second term in Eq. (9) using Eq. (10) with either the experimental data or our theory for δT_c yields variability in $\delta\lambda_{ab}/\lambda_{ab}$ on the order of 0.1% among the samples with depressed T_c. The variation in $\delta\lambda_{ab}/\lambda_{ab}$ with T_c is therefore predicted to be negligible and is in agreement with experiment, where scatter in the data comprises a larger uncertainty of $(0.7 \pm 0.4)\%$.

The upturn in $\delta\lambda_{ab}/\lambda_{ab}$ for $\delta T_c/T_c \geqslant 0.03$, indicated by the dashed line in Fig. 3, corresponds to samples where T_c is depressed by 50% or more and the superconducting transitions are notably broadened. A likely scenario is that the superconductivity in these materials is macroscopically inhomogeneous, perhaps analogous to the striped phase in underdoped materials, which also have a strongly depressed T_c. Although the microstructure of the inhomogeneity has not been determined, one may presume that it comprises superconducting and normal phases and interfaces between them, such as the "striped phase" observed where superconductivity is strongly degraded.[41] This regime bears some analogy to the proximity systems studied by Kresin *et al.*, who modeled the OIE for juxtaposed superconducting and normal layers.[14] These authors found that the OIE increases monotonically with the ratio of normal to superconducting layer thickness. Given the experimental observations, this approach appears to be relevant in understanding samples with strongly depressed T_c.

IV. DISCUSSION

The most striking features of the OIE in the high-T_c materials are that (1) it tends to zero for superconductors approaching optimal stoichiometry and (2) the substitution $^{16}\mathrm{O} \rightarrow {}^{18}\mathrm{O}$ results in a lower T_{c0}. Some authors (see, e.g., Refs. 42 and 43) have advocated a phonon-based perspective, noting the large OIE observed for nonoptimum stoichiometry can be even larger than the BCS expectation of $\alpha_{\mathrm{O}} = 0.5$. However, this point of view ignores the degradation in the superconducting condensate that accompanies the introduction of substitutional disorder. Thus, a large OIE is merely indicative of a poor quality condensate, where measurements of normally intrinsic quantities such as the penetration depth provide only "effective" values (rendering a determination of n_s/m_{ab}^* impossible). Indeed, if the pairing mechanism were truly polaronic (or phononic) in nature, one would expect the OIE to increase in magnitude upon approaching the optimal high-T_c state. Since experiments show that the reverse is true and that phonons cannot explain the high transition temperatures, one might at this point confidently conclude that polaronic interactions are noncentral to the high-T_c pairing mechanism. Note that even the optimum high-T_c materials have inherent lattice disorder, either because of alloy doping, as in the case of $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$, or because of the presence of randomly distributed oxygen vacancies, as in $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$. This crystalline disorder potentially creates some measure of pair breaking, given the short coherence distance in these high-T_c superconductors.

Nevertheless, several authors[10–13] resurrected the idea of phonon mediation in the form of small polarons.[6] Based on the incorrect premise that Pr dopes only the Y sites in Pr-doped $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ (i.e., ignoring Pr-on-Ba-site defects), the authors of Refs. 10–13 erroneously concluded that (1) the superconducting hole condensate is located in the CuO_2 planes and (2) the superconductivity mechanism is associated with phonon effects, specifically, small polarons. However, since pair breaking occurs in the presence of Pr-on-Ba-site defects, and not for Pr-on-Y-site substitution in Pr-doped $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$, the site-specific OIE data of Fig. 2, which show the absence of an OIE in the apical and chain oxygens, provides the definitive evidence against phonon-based pairing.

More than just providing evidence against misguided hypotheses, the data in Fig. 2 show unambiguously that the charged carriers in the CuO_2 planes are sensitive to changes in the number density of the charge carriers located in the BaO layers. In other words, the carriers in the BaO layers interact with those in the CuO_2 planes.

Ignoring Pr-on-Ba-site defects in the above experimental studies[10–13] has also adversely affected early theoretical development, particularly those efforts attempting to explain high-T_c superconductivity phenomena in terms of nonadiabaticity in the electron-phonon interaction.[14–18,44] The corrected description of experimental samples and the results obtained thereupon suggest reexamining of the theoretical premise (i.e., that Pr substitutes only for the Y). While previous treatments of nonadiabaticity may be applicable to understanding the OIE in the penetration depth,[44] and some aspects of BCS-like electron-phonon interactions[45] may be relevant to nonoptimum materials, the high-T_c compounds are clearly not phonon mediated. Indeed, a correct theory of the OIE in T_c requires the inclusion of the pairing mechanism, i.e., Coulomb interactions among carriers in BaO and CuO_2 layers (in the case of $YBa_2Cu_3O_{7-\delta}$), and pair-breaking effects.

Our approach to the OIE problem, therefore, begins with the assumption that pair breaking arising from disorder is primarily responsible for the suppression of T_c in all cation substituted samples. With the added knowledge of Pr-on-Ba-site defects, all of the data presented in Fig. 1 are completely explained using a straightforward pair-breaking model with a scattering-induced enhancement of the OIE that arises from heterovalent substitution. We have generalized the more restrictive model of Ref. 14 to cover all cases, heterovalent, isovalent, and nonmagnetic substitutions. For isovalent $Zn^{+2} \rightarrow Cu^{+2}$ and $Sr^{+2} \rightarrow Ba^{+2}$ substitutions, the OIE follows a standard pair-breaking T dependence given by Eq. (7a). However, in the case of the underdoped materials such as Pr^{+3} and La^{+3} substituting for Ba^{+2}, the enhancement factor associated with heterovalent substitution given in Eq. (7b) becomes important.

Pair breaking also gives a consistent explanation for the increase in penetration depth and concomitant decrease in T_c with cation substitution. Moreover, the OIE in the penetration depth, $\alpha_{O,\lambda}$, is independent of T_c over a significant range $\frac{1}{2}T_{c0} < T_c \leqslant T_{c0}$, indicating its independence of pair breaking over a broad variation of T_c. In the region $T_c < \frac{1}{2}T_{c0}$ (corresponding to $\delta T_c / T_c > 3\%$ in Fig. 3), the studied materials approach the metal-insulator transition, where the degradation of the superconducting state becomes significant. Material changes substantiated by greatly broadened transition widths[9,41] or the presence of striped phases[41] render λ_{ab} and $\delta\lambda_{ab}$ nonamenable to quantitative analysis in terms of either carrier concentration or effective mass.

Our unique approach explains all of the OIE data self-consistently in terms of scattering enhanced pair breaking and is valid for all high-T_c materials. The OIE in $Bi_2Sr_2CaCu_2O_{8+\delta}$ shows similar trends, wherein deviations from the optimum δ (where $T_{c0}=89$ K) leads to depressed and broadened superconducting transitions with enhanced OIE. From Fig. 1 of Ref. 40, we estimate $\alpha_O \approx 0.092$ for an overdoped sample with $T_c \approx 71.8$ K. Equation (7b) predicts $\alpha_O = 0.10$. This close agreement is consistent with the strong pair-breaking picture, in that oxygen overdoping yields the same effect as heterovalent cation substitution. While a more complex OIE behavior is found in $La_{2-x}Sr_xCuO_4$, probably because T_{c0} is nonunique (a satellite T_{c0} appears at $x \sim 0.09$), the unmistakable experimental finding is that departures from optimal x (either 0.09 or 0.16) lead to increases in α_O by up to a factor of 10 (see Fig. 6 of Ref. 10). The heterovalency difference between La^{+3} and Sr^{+2} and pair breaking combine to enhance α_O. The behavior is described by Eq. (7b) and suggests perturbation of hole carriers in SrO layers. In the case of κ-$[\text{BEDT-TTF}]_2\text{Cu}[\text{NCS}]_2$ (κ-$[\text{bis(ethylenedithiolo-)tetrathiafulvalene}]_2\text{Cu}[\text{NCS}]_2$), the mobile holes are located in the sulfur chains of the BEDT-TTF molecule and the mediating electrons are in the (normal) $\text{Cu}[\text{NCS}]_2$ anion layers. Isotope effect measurements[46,47] conducted on this material have shown conclusively that the substitution $^{32}S \rightarrow {}^{34}S$ in the cation BEDT-TTF molecule induces no measurable isotope effect. This is analogous to the absence of an OIE in the BaO layers of $YBa_2Cu_3O_{7-\delta}$.

Further consideration of carriers in the BaO and CuO_2 layers may elucidate the true nature of the pairing interaction. Specific heat data in the high-T_c materials exhibit a linear-in-T term,[48] while the low-temperature thermal conductivity κ features a corresponding offset in κ/T from zero.[49,50] Since the gap function of $YBa_2Cu_3O_{7-\delta}$ is nodeless,[27,28] this behavior cannot be related to the pairing symmetry, and thus reflects the presence of normal excitations below T_c in the high-T_c superconductors[48] (i.e., some layers contain normal carriers). Signatures of d-state symmetry seen in scanning tunneling microscopy[51] and photoemission[52,53] data, which is not reflected in the μ^+SR (muon spin rotation) analysis,[27,28] must then be associated with the normal state carriers. Given this and the interaction shown to exist between the BaO and CuO_2 layers shown in Fig. 2, we conclude that the high-T_c pairing mechanism is Coulomb based, involving interactions between hole and electron layers. In the case of $YBa_2Cu_3O_{6.95}$, BVS calculations[35] indicate that mobile holes are most likely found in the BaO layers or in the CuO chains. The CuO chains are ruled out, however, owing to the s-wave character of the pairing state (i.e., no Cu d-band signature), and the decrease in the CuO charge with increasing oxygen content in $YBa_2Cu_3O_{7-\delta}$.[35] Thus, electrons in the cuprate planes must mediate the pairing of holes in the BaO layers.[54] We suggest previous theoretical treatments of the OIE, which embrace the notion that the CuO_2 planes that have mobile holes[14–18,44,45] be reconsidered.

V. CONCLUSIONS

We have shown that the conclusions reached by Keller and co-workers[10–13] based on Pr-doped $YBa_2Cu_3O_{7-\delta}$ samples containing significant Pr-on-Ba-site defects are without merit. There is clearly no evidence supporting polaronic or any other known phonon-based mediation in the high-T_c materials. Most importantly, the site-specific OIE data shown in Fig. 2 provide evidence that the mobile carriers in the CuO_2 planes interact with those in the BaO planes, indicating that Coulomb forces are important. Given these facts and further hypothesizing that the electron-phonon scattering (associated with heterovalent substitution) scales with the pair-breaking rate, the OIE in T_c observed in the high-T_c materials reduces to Eqs. (7a) and (7b). Moreover, we have also shown that the OIE observed in the magnetic penetration depth is nearly independent of T_c (for T_c depressed by up to 50%), which is consistent with its originating from the OIE in normal state properties, such as effective mass and carrier concentration. Since specific heat and thermal conductivity data provide evidence for a pool of normal electrons and BVS calculations make it difficult to place the mobile holes in the CuO_2 planes, we propose a Coulomb-based mediation mechanism, where holes in the BaO, SrO, etc., layers are mediated by electrons in the CuO_2 (or equivalent anion) planes.[54] Our model is found to be in agreement with isotope effect experiments on κ-[BEDT-TTF$]_2$Cu[NCS$]_2$, $La_{2-x}Sr_xCuO_4$, and $YBa_2Cu_3O_{7-\delta}$, which span a range in T_{c0} from 10 to 90 K.

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[1] D. R. Harshman and A. P. Mills, Jr., Phys. Rev. B **45**, 10684 (1992); D. R. Harshman, in *Proceedings of the International School of Physics, Enrico Fermi Course CXXV on Positron Spectroscopy of Solids*, Varenna, Italy, 6–16 July 1993 (IOS Press, Amsterdam, 1995).

[2] E. Maxwell, Phys. Rev. **78**, 477 (1950).

[3] C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt, Phys. Rev. **78**, 487 (1950).

[4] S. Hoen, W. N. Creager, L. C. Bourne, M. F. Crommie, T. W. Barbee, III, M. L. Cohen, A. Zettl, L. Bernardez, and J. Kinney, Phys. Rev. B **39**, 2269 (1989).

[5] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[6] A. S. Alexandrov, in *Polarons in Advanced Materials*, edited by A. S. Alexandrov (Springer-Verlag, Berlin, 2007).

[7] M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987).

[8] M. Gurvitch, A. T. Fiory, L. F. Schneemeyer, R. J. Cava, G. P. Espinosa, and J. V. Waszczak, Physica C **153-155**, 1369 (1988).

[9] G. Soerensen and S. Gygax, Phys. Rev. B **51**, 11848 (1995).

[10] H. Keller, Struct. Bonding (Berlin) **114**, 143 (2005).

[11] R. Khasanov, A. Shengelaya, E. Morenzoni, M. Angst, K. Conder, I. M. Savić, D. Lampakis, E. Liarokapis, A. Tatsi, and H. Keller, Phys. Rev. B **68**, 220506(R) (2003); G.-M. Zhao, K. Conder, H. Keller, and K. A. Müller, J. Phys.: Condens. Matter **10**, 9055 (1998).

[12] R. Khasanov, D. G. Eshchenko, H. Luetkens, E. Morenzoni, T. Prokscha, A. Suter, N. Garifianov, M. Mali, J. Roos, K. Conder, and H. Keller, Phys. Rev. Lett. **92**, 057602 (2004).

[13] R. Khasanov, A. Shengelaya, K. Conder, E. Morenzoni, I. M. Savić, and H. Keller, J. Phys.: Condens. Matter **15**, L17 (2003).

[14] V. Z. Kresin, A. Bill, S. A. Wolf, and Y. N. Ovchinnikov, Phys. Rev. B **56**, 107 (1997).

[15] A. Bill, V. Z. Kresin, and S. A. Wolf, Phys. Rev. B **57**, 10814 (1998).

[16] A. Deppeler and A. J. Millis, Phys. Rev. B **65**, 224301 (2002).

[17] P. Paci, M. Capone, E. Cappelluti, S. Ciuchi, C. Grimaldi, and L. Pietronero, Phys. Rev. Lett. **94**, 036406 (2005).

[18] L. Pietronero, S. Strässler, and C. Grimaldi, Phys. Rev. B **52**, 10516 (1995).

[19] J. P. Franck, J. Jung, M. A.-K. Mohamed, S. Gygax, and G. I. Sproule, Phys. Rev. B **44**, 5318 (1991).

[20] J. P. Franck, J. Jung, M. A.-K. Mohamed, S. Gygax, and G. I. Sproule, Physica B **169**, 697 (1991); J. C. Phillips, Phys. Rev. B **43**, 6257 (1991); C. L. Seaman, J. J. Neumeier, M. B. Maple, L. P. Le, G. M. Luke, B. J. Sternlieb, Y. J. Uemura, J. H. Brewer, R. Kadono, R. F. Kiefl, S. R. Krietzman, and T. M. Riseman, *ibid.* **42**, 6801 (1990). The behavior exhibited by these data was first attributed to disordering effects in 1992 (Ref. 1).

[21] H. A. Blackstead and J. D. Dow, Phys. Rev. B **51**, 11830 (1995); M. P. Nutley, A. T. Boothroyd, and G. J. McIntyre, J. Magn. Magn. Mater. **104-107**, 623 (1992).

[22] Z. Zou, K. Oka, T. Ito, and Y. Nishihara, Jpn. J. Appl. Phys., Part 2 **36**, L18 (1997).

[23] A. Shukla, B. Barbiellini, A. Erb, A. Manuel, T. Buslaps, V. Honkimäki, and P. Suortti, Phys. Rev. B **59**, 12127 (1999).

[24] F. M. Araujo-Moreira, P. N. Lisboa-Filho, A. J. C. Lanfredi, W. A. Ortiz, S. M. Zanetti, E. R. Leite, A. W. Morbru, L. Ghivelder, Y. G. Zhao, and V. Venkatesan, Physica C **341-348**, 413 (2000).

[25] F. M. Araujo-Moreira, P. N. Lisboa-Filho, S. M. Zanetti, E. R. Leite, and W. A. Ortiz, Physica B **284-288**, 1033 (2000).

[26] For a review, see H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).

[27] D. R. Harshman, W. J. Kossler, X. Wan, A. T. Fiory, A. J. Greer, D. R. Noakes, C. E. Stronach, E. Koster, and J. D. Dow, Phys. Rev. B **69**, 174505 (2004).

[28] D. R. Harshman, W. J. Kossler, X. Wan, A. T. Fiory, A. J. Greer, D. R. Noakes, C. E. Stronach, E. Koster, and J. D. Dow, Phys. Rev. B **72**, 146502 (2005).

[29] J. D. Dow and D. R. Harshman, in *New Challenges in Superconductivity: Experimental Advances and Emerging Theories*, edited by J. Ashkenazi, M. V. Eremin, J. L. Cohn, I. Eremin, D. Manske, D. Pavuna, and F. Zuo, NATO Science Series II: Mathematics, Physics and Chemistry (IOS, Amsterdam/Springer, New York, 2005), Vol. 183, pp. 129–134.

[30] J. D. Dow, D. R. Harshman, and A. T. Fiory, in *Electron Correlations in New Materials and Nanosystems*, edited by K. Scharnberg and S. Kruchinin, NATO Science Series II: Mathematics, Physics and Chemistry (Springer, Berlin, 2007), Vol. 241, pp. 263–274.

[31] G.-M. Zhao and D. E. Morris, Phys. Rev. B **51**, 16487 (1995).

[32] H. J. Bornemann and D. E. Morris, Phys. Rev. B **44**, 5322 (1991).

[33] B. Lake, G. Aeppli, K. N. Clausen, D. F. McMorrow, K. Lefmann, N. E. Hussey, N. Mangkorntong, M. Nohara, H. Takagi, T. E. Mason, and A. Schröder, Science **291**, 1759 (2001).

[34] M. K. Crawford, M. N. Kunchur, W. E. Farneth, E. M. McCarron, III, and S. J. Poon, Phys. Rev. B **41**, 282 (1990).

[35] I. D. Brown, J. Solid State Chem. **82**, 122 (1989); O. Chmaissem, Y. Eckstein, and C. G. Kuper, Phys. Rev. B **63**, 174510 (2001).

[36] M. Tinkham, *Introduction to Superconductivity*, 2nd ed. (McGraw-Hill, New York, 1996), Chap. 8.

[37] A. F. Hebard and M. A. Paalanen, Phys. Rev. B **30**, 4063 (1984).

[38] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical*

Functions (Dover, New York, 1965), Chap. 6.

[39] J. L. Tallon, J. W. Loram, J. R. Cooper, C. Panagopoulos, and C. Bernhard, Phys. Rev. B **68**, 180501(R) (2003). Similar conclusions were reached earlier in Ref. 1.

[40] D. J. Pringle, G. V. M. Williams, and J. L. Tallon, Phys. Rev. B **62**, 12527 (2000).

[41] H. A. Mook, Pengcheng Dai, and F. Doğan, Phys. Rev. Lett. **88**, 097004 (2002).

[42] M. K. Crawford, W. E. Farneth, E. M. McCarron, III, R. L. Harlow, and A. H. Moudden, Science **250**, 1390 (1990).

[43] J. P. Franck, S. Gygax, G. Soerensen, E. Altshuler, A. Hnatiw, J. Jung, M. A.-K. Mohamad, M. K. Yu, G. I. Sproule, J. Chrzanowski, and J. C. Irwin, Physica C **185-189**, 1379 (1991).

[44] C. Grimaldi, E. Cappelluti, and L. Pietronero, Europhys. Lett. **42**, 667 (1998).

[45] X.-J. Chen, V. Struzhkin, Z. Wu, H.-Q. Lin, R. J. Hemley, and H.-K. Mao, Proc. Natl. Acad. Sci. U.S.A. **104**, 3732 (2007).

[46] K. D. Carlson, A. M. Kini, J. A. Schlueter, U. Geiser, R. A. Klemm, J. M. Williams, J. D. Dudek, M. A. Caleca, K. R. Lykke, H. H. Wang, J. A. Ferraro, and P. Stout, Physica C **215**, 195 (1993).

[47] A. M. Kini, K. D. Carlson, H. H. Wang, J. A. Schlueter, J. D. Dudek, S. A. Sirchio, U. Geiser, K. R. Lykke, and J. M. Williams, Physica C **264**, 81 (1996).

[48] K. A. Moler, D. L. Sisson, J. S. Urbach, M. R. Beasley, A. Kapitulnik, D. J. Baar, R. Liang, and W. N. Hardy, Phys. Rev. B **55**, 3954 (1997).

[49] L. Taillefer, B. Lussier, R. Gagnon, K. Behnia, and H. Aubin, Phys. Rev. Lett. **79**, 483 (1997).

[50] D. R. Harshman and J. D. Dow, Mod. Phys. Lett. B **19**, 147 (2005).

[51] S. H. Pan, J. P. O'Neal, R. L. Badzey, C. Chamon, H. Ding, J. R. Engelbrecht, Z. Wang, H. Eisaki, S. Uchida, A. K. Gupta, K.-W. Ng, E. W. Hudson, K. M. Lang, and J. C. Davis, Nature (London) **413**, 282 (2001).

[52] A. Damascelli, Z.-X. Shen, and Z. Hussain, Rev. Mod. Phys. **75**, 473 (2003).

[53] J. C. Campuzano, M. R. Norman, and M. Randeria, in *Physics of Superconductors*, edited by K. H. Benneman and J. B. Ketterson (Springer, Berlin, 2004), Vol. 2, pp. 167–273.

[54] D. R. Harshman, J. D. Dow, and A. T. Fiory (unpublished).