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Superconducting-state enhancement of thermal conductivity in the cuprates: Correlation with the pair density

Joshua L. Cohn
Department of Physics, University of Miami, Coral Gables, Florida 33124

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The systematics of the superconducting-state enhancements of in-plane thermal conductivity for $YBa_2Cu_3O_{6+x}$ (Y-123), $Bi_2Sr_2CaCu_2O_8$, $Tl_2Ba_2CuO_6$, and $La_{2-x}Sr_xCuO_4$ single crystals are examined. For Y-123 the enhancements are shown to correlate with specific-heat jumps, a measure of the superconducting pair density. The substantially larger enhancements observed for Y-123 are attributed to the condensate arising from oxygen-filled CuO chains. We discuss the constraints imposed by measurements of microwave conductivity on the electronic contribution to this phenomenon.

Considerable attention has been focused recently on the in-plane thermal conductivity (κ_{ab}) of cuprate superconductors.[1] In the superconducting state ($T<T_c$), κ_{ab} rises above its normal-state value and reaches a material-dependent maximum at $T_{\max}$ with $0.4 \leqslant T_{\max}/T_c \leqslant 0.8$. Both phononic and electronic mechanisms have been proposed to explain this enhancement but there is currently no consensus regarding its origin.[2–8] A phononic explanation may be viewed as "conventional" in that for disordered superconductors such as $Pb_{0.9}Bi_{0.1}$,[9] NbC,[10] and $Zr_{70}Cu_{30}$,[11] a similar peak occurs, attributed to a reduction in phonon-carrier scattering as the charge carriers condense in the superconducting state. An electronic mechanism entails a dramatic enhancement in the quasiparticle lifetime, τ_{qp}, in the superconducting state, so as to overcome a decreasing number of quasiparticle excitations. In support of an electronic scenario are the microwave conductivity derived from the measured surface resistance,[12] which implies such an enhancement in τ_{qp}, and theoretical models for the cuprates wherein scattering by spin fluctuations and d-wave pairing are central ingredients.[3,5,13]

Though many measurements of κ_{ab} for single-crystal specimens have been reported, a comparative survey of the enhancement systematics for different materials, and particularly its dependence on charge-carrier doping, has not been presented. In this paper we examine the available data for four compounds: $YBa_2Cu_3O_{6+x}$ (Y-123), $Bi_2Sr_2CaCu_2O_8$ (Bi-2212), $Tl_2Ba_2CuO_6$ (Tl-2201), and $La_{2-x}Sr_xCuO_4$ (LSCO). For Y-123, where sufficient data are available, we demonstrate that the magnitude of the enhancement is proportional to the superconducting pair density, n_s. The implications of this finding for interpretations of the enhancement are discussed.

Since the enhancement arises from a reduction in scattering, we describe it by the normalized change in the in-plane thermal resistivity at $T_{\max}$, $\delta W/W \equiv [W^n_{ab}(T_{\max}) - W^s_{ab}(T_{\max})]/W^n_{ab}(T_{\max}) = 1 - \kappa^n_{ab}(T_{\max})/\kappa^s_{ab}(T_{\max})$, where $\kappa^n_{ab}(T_{\max})$ and $\kappa^s_{ab}(T_{\max})$ are the normal- and superconducting-state thermal conductivities, respectively, and the W_{ab} represent corresponding thermal resistivities. $\kappa^n_{ab}(T_{\max})$ is estimated by extrapolating the normal-state data to $T_{\max}$. In most cases (such as for optimally doped Y-123 and Tl-2201) κ_{ab} is a weak function of temperature for $T>T_c$, and thus $\kappa^n_{ab}(T_{\max}) \simeq \kappa_{ab}(T_c)$. For Bi-2212 and underdoped Y-123 the normal-state T dependence is more marked, and the use of $\kappa^n_{ab}(T_{\max})$ rather than $\kappa_{ab}(T_c)$ in defining $\delta W/W$ more aptly reflects the enhancement due to superconductivity alone. $\delta W/W$ is independent of geometric uncertainties (typically 10–20 %) that are inherent in all measurements of small crystals.

Figure 1 shows $\delta W/W$ plotted versus $T_{\max}/T_c$ for single crystals of the four compounds Y-123,[8,14–25] Bi-2212,[7,22,26–29] Tl-2201,[30] and LSCO.[31,32] This figure highlights two aspects of the enhancement systematics: (1) $\delta W/W \sim 0.1 - 0.2$ represents a lower bound for all of these materials, and (2) Y-123 *is unique* in that its $\delta W/W$ values vary widely and can substantially exceed 0.2, with larger enhancements occurring at lower temperatures. It is immediately clear from this figure that $\delta W/W$ *does not* correlate universally with the hole concentration in the CuO_2 planes (p) since all of the specimens represented, with the exception of two LSCO samples, were near optimal doping ($0.13 \leqslant p \leqslant 0.19$).

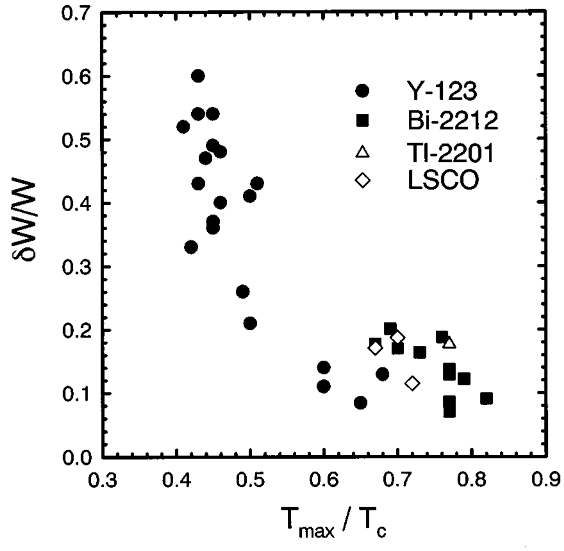

FIG. 1. $\delta W/W$ vs $T_{\max}/T_c$ for cuprate crystals.

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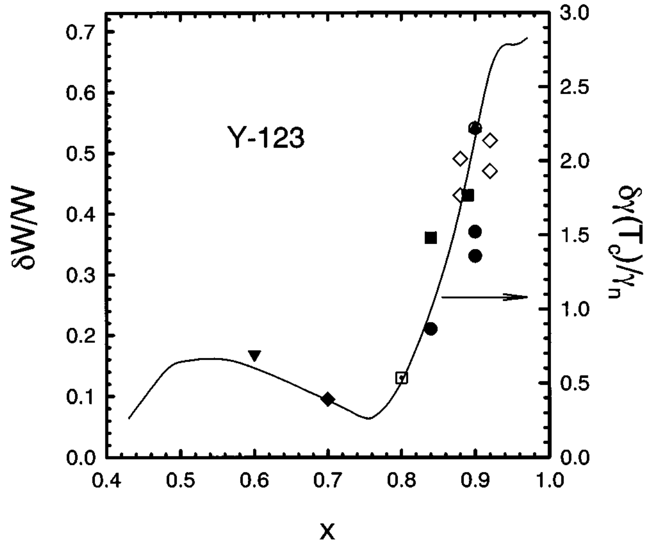

FIG. 2. $\delta W/W$ vs x for Y-123 crystals. The open symbols are for untwinned specimens from Ref. 20 (diamonds) and Ref. 23 (circles); the larger (smaller) $\delta W/W$ values for each pair of open symbols correspond to heat flow along the *a* axis (*b* axis). The remaining symbols are for twinned specimens from Ref. 15 (dotted square), Ref. 16 (diamond), Ref. 18 (squares), Ref. 19 (circles), Ref. 22 (inverted triangle), and Ref. 23 (triangle). The solid line is the normalized electronic specific heat jump for polycrystals, adapted from Ref. 38.

The data of Henning *et al.*[24] confirm that the large variations in $\delta W/W$ for Y-123 are principally due to differences in oxygen content. Their as-grown Y-123 crystal, with $\delta W/W=0.08$, was subsequently annealed in oxygen at high pressure and remeasured, yielding $\delta W/W=0.46$. Though oxygen content was not specified, for both oxygenation states $T_c \geqslant 92$ K, indicating $0.8 \leqslant x \leqslant 1.0$ (i.e., within the "90 K plateau"). Values of $\delta W/W$ larger than 0.2 for Y-123 are thus associated with the filling of oxygen vacancies on the CuO chains.

The oxygen-doping dependence of the enhancement in Y-123 is shown in Fig. 2 where we plot $\delta W/W$ vs x for that subset of Fig. 1 measurements for which values of x were reported. Also included in this figure are data (dotted square) from Ref. 15 with oxygen content estimated from the $T_c(x)$ phase curve[33,34] using the suppressed T_c value (88 K). The largest uncertainties in this plot are for the oxygen content. In some cases[18–20] these values were determined from the thermopower,[34,35] magnetization,[36] and/or lattice parameters[37] measured on the same crystals, but in others the method was unspecified. Uncertainties in x and oxygen homogeneity may account for the scatter in the data.

It is now well established from measurements of the specific heat[38] and penetration depth[39,40] that fully oxygenated chains in Y-123 are superconducting and contribute substantially to the condensate density (n_s). It is remarkable that $\delta W/W$ follows closely the normalized electronic specific heat jump, $\delta\gamma(T_c)/\gamma_n \propto n_s/n$, from Loram *et al.*[38] (solid line in Fig. 2). The most dramatic feature in $\delta\gamma(T_c)/\gamma_n$ is its increase by nearly an order of magnitude within the 90 K plateau,[38,41] indicating a corresponding enhancement in pair density, arising principally from the chains. A second feature, the local maximum, corresponds to the 60 K plateau, where the chains are alternately full and empty. These data support a model in which superconductivity extends to oxygen-filled chains via the proximity effect, and is suppressed by pair breaking on disordered chains due to vacancy-induced local moments.[39,42] Both the 90 K and 60 K features are evident in $\delta W/W$, though further measurements for heavily underdoped crystals are needed to convincingly establish the second feature. The same qualitative behavior of $\delta W/W$ with x has been confirmed in systematic measurements on individual polycrystal Y-123 specimens.[43] The available data for crystals of the other materials are insufficient[44] to construct plots similar to Fig. 2.

To interpret the results of Fig. 2 we must consider both electronic (κ_e) and lattice (κ_L) contributions to the heat flow, $\kappa=\kappa_e+\kappa_L$ (we speak exclusively of the in-plane thermal conductivity, and omit the *ab* subscript without confusion). Thus, $\delta W/W=1-(\kappa_e^n+\kappa_L^n)/(\kappa_e^s+\kappa_L^s)$. Qualitatively, we can see that the behavior $\delta W/W \propto n_s/n$ can arise from either a phononic or electronic mechanism if the enhancement in one of these contributions predominates. When Matthiessen's rule is obeyed,[45] the normal- and superconducting-state thermal resistivities (at temperature $T_{\max}$) for either electronic or lattice heat flow can be expressed as $W^n=A+B$ and $W^s=A(1-n_s/n)+B$, respectively, where A represents charge-carrier scattering and B all other scattering. This two-fluid scheme for the superconducting state yields $\delta W/W=[A/(A+B)](n_s/n)$, in qualitative agreement with the data, provided the ratio $A/(A+B)$ is a weak function of doping. More generally, enhancements in both κ_e and κ_L imply a more complex behavior for $\delta W/W$, with higher-order terms in n_s/n. In addition, the scattering parameters may be expected to change with doping. For example, κ_L for insulating Y-123 is extremely sensitive to small variations in oxygen content.[46] Thus, a general treatment of $\delta W/W$ entails model-dependent assumptions.

Constraints on an electronic enhancement can be found by considering measurements of other electronic properties. Observations of a peak near $T_{\max}$ in the microwave conductivity, σ_1,[12] provide motivation for the proposal[47] that κ_e^s scales with σ_1 according to the Wiedemann-Franz relation, and tend to support an electronic mechanism for the enhancement. If inelastic scattering is rapidly suppressed at $T<T_c$, the quasiparticle transport might be expected to obey, $\kappa_e^s(T)=TL^s\sigma_1(T)$, with the quasiparticle Lorenz number near its ideal value for elastic scattering, $L^s \simeq L_0=2.45\times10^{-8} W\Omega/K^2$. Theory[48] does not support this relationship, but experimentally it is approximately followed for untwinned Y-123 near optimal doping if it is assumed[47] that there is no enhancement in κ_L, i.e., $\kappa_L^s=\kappa_L^n$.

Systematic studies of microwave surface resistance (R_s),[49] penetration depth (λ),[39] and normal-state electrical conductivity (σ^n) (Ref. 50) as functions of x for Y-123, allow for a more stringent test of the scaling of κ_e^s with σ_1. Taking $\kappa_e^s=T_{\max}L^s\sigma_1$, $\kappa_e^n=T_{\max}L^n\sigma^n$, and assuming $\kappa_L^s=\kappa_L^n$, the doping-dependent *electronic* enhancement can be expressed as

$$\frac{\delta W}{W}(x)=1-\left\{\frac{L^s\sigma^n(x)T_{\max}}{\kappa^n(x)}\left[\frac{\sigma_1(x)}{\sigma^n(x)}-\frac{L^n}{L^s}\right]+1\right\}^{-1}, \quad (1)$$

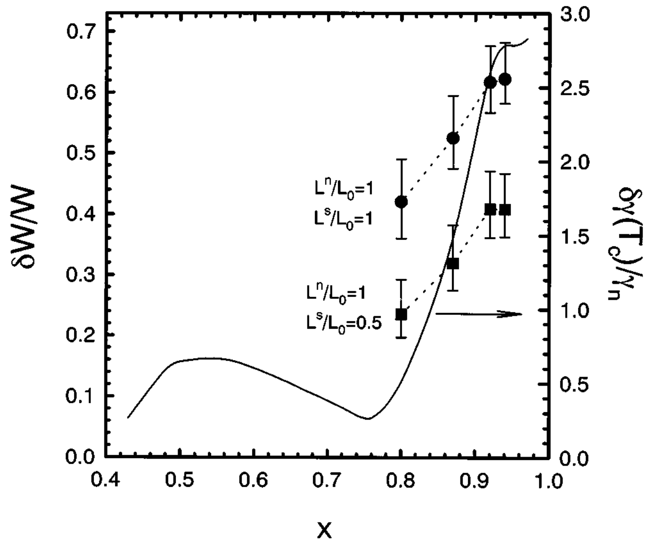

FIG. 3. Electronic contribution to $\delta W/W$ computed from the microwave conductivity of Ref. 49 using Eq. (1) and Lorenz numbers as indicated. The solid line and scaling of axes are the same as in Fig. 2.

where all quantities are to be evaluated at $T_{\max}$. We assume initially that L^s and L^n are independent of x. Bonn *et al.*[49] observed a peak in R_s at $T_{\max}=40$ K that was independent of oxygen content ($R_s=30$ $\mu\Omega$ at $\omega/2\pi=3.64$ GHz) for four x values[51] of the same crystal. Using these results and $\lambda(x)$,[39] we compute $\sigma_1(x)=(2/\mu_0^2\omega^2)R_s/\lambda^3(x)$. σ^n is found by linear-T extrapolation of the normal-state resistivity.[50] Systematic measurements of $\kappa(x)$ on an individual crystal for this x range are not available, so we rely on the following estimate for $\kappa^n(x)$. For the highest oxygen content ($x=0.94$) we take $\kappa^n(0.94)=12.3\pm2.6$ W/mK, the average (and standard deviation for uncertainty) of sixteen specimens from the literature (Fig. 1) having $T_c\geqslant90$ K and $T_{\max}\leqslant45$ K. For subsequent values of x this κ^n is reduced according to the Wiedemann-Franz relation to account for the decrease in κ_e^n, i.e., $\kappa^n(x)=\kappa^n(0.94)-T_{\max}L^n[\sigma^n(0.94)-\sigma^n(x)]$. Results using $L^s=L^n=L_0$ for all x are shown in Fig. 3 (circles).

The computed and measured $\delta W/W$ are in reasonable accord for $x\geqslant0.9$, but the former overestimates the latter by a factor of 3 near $x=0.8$. This disagreement is well outside any uncertainties introduced in our analysis. Allowing enhancements in κ_L increases the discrepancy, as does incorporating a decrease in κ_L^n with decreasing x implied by polycrystal studies.[43,52] We consider two possible conclusions from these results that may resolve the apparent discrepancy: (1) L^n and L^s at $T_{\max}$ differ from L_0 and may vary with x, and (2) κ_e does not follow σ_1 and the enhancement in κ_L predominates for all x.

The first point to note regarding the Lorenz ratios is that $\sigma_1/\sigma^n\simeq7-8$ for all x, and thus $\delta W/W$ as computed from Eq. (1) is rather insensitive to the value of L^n. Thus, L^s *must decrease below* L_0 with decreasing x to account for the behavior of $\delta W/W(x)$. For purely elastic scattering and in the clean limit (appropriate to Y-123), both strong and weak coupling for a single s-wave gap yield $L^s>L_0$ at $T_{\max}$.[53] Recent computations for two-dimensional, $d_{x^2-y^2}$-wave superconductors[48] indicate $0.5\leqslant L^s/L_0\leqslant1.5$ in the clean limit, with larger (smaller) values corresponding to unitarity (Born) impurity scattering. In Fig. 3 we show $\delta W/W$ computed from (1) using $L^n=L_0$, $L^s=L_0/2$ (squares). This curve represents a lower bound on an electronic contribution for the $d_{x^2-y^2}$-wave case. Better agreement with the doping dependence (but not the magnitude) is possible if $L^s(x)$ is allowed to vary continuously from 1.5 at $x=0.94$ to 0.5 at $x=0.80$. Within the $d_{x^2-y^2}$-wave model of Graf *et al.* such a variation in L^s implies an impurity scattering strength that decreases from strong to weak with decreasing x. This would appear to be inconsistent with the d-wave theory for the microwave response,[13] the predictions of which are incompatible with experiment[12] in the weak-scattering limit. The presence of residual inelastic scattering at $T_{\max}$ would not alter these conclusions.

Alternatively, it is possibile that the peak in σ_1 has nothing to do with scattering, i.e., does not imply a τ_{qp} that grows dramatically below T_c. There is theoretical motivation for this point of view. Calculations[54] of σ_1 from Eliashberg theory with a two-gap model[42] yield a peak in σ_1 independent of the form of τ_{qp}. Thus the enhancement in κ_e could be negligible and $\delta W/W$ predominantly phononic. The doping dependence in Fig. 2 could then be interpreted conventionally.

In conclusion, we have shown that the superconducting-state enhancement of the in-plane thermal conductivity for Y-123 correlates with the pair density, and that the uniquely large enhancements observed in this material are associated with the condensate arising from the CuO chains. The doping dependence of the enhancement is inconsistent with an electronic mechanism and a quasiparticle thermal conductivity that scales with the microwave conductivity according to the Wiedemann-Franz relation. Measurements of λ, σ_1, and κ for $x<0.8$ in Y-123 should further constrain an electronic scenario. Doping-dependent studies of κ for cuprates without chains, and extending into the overdoped regime, should help to clarify the generality of our observations.

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[1] C. Uher, in *Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1993), Vol. III.

[2] J. L. Cohn *et al.*, Phys. Rev. Lett. **71**, 1657 (1993).

[3] R. C. Yu, M. B. Salamon, and J. P. Lu, Phys. Rev. Lett. **71**, 1658 (1993).

[4] A. S. Alexandrov and N. F. Mott, Phys. Rev. Lett. **71**, 1075 (1993).

[5] B. W. Statt and A. Griffin, Phys. Rev. B **48**, 619 (1993).

[6] W. S. Williams, Solid State Commun. **87**, 355 (1993).

[7] P. B. Allen *et al.*, Phys. Rev. B **49**, 9073 (1994).

[8] C. Uher, Y. Liu, and J. F. Whitaker, J. Supercond. **7**, 323 (1994).

[9] K. Mendelssohn and J. L. Olsen, Proc. Phys. Soc. London **63A**, 2 (1950).

[10] L. G. Radosevich and W. S. Williams, Phys. Rev. **188**, 770 (1970).

[11] P. Esquinazi and F. de la Cruz, Phys. Rev. B **27**, 3069 (1983).

[12] D. A. Bonn *et al.*, Phys. Rev. Lett. **68**, 2390 (1992); D. A. Bonn *et al.*, Phys. Rev. B **47**, 11 314 (1993); D. A. Bonn *et al.*, *ibid.* **50**, 4051 (1994); K. Zhang *et al.*, Phys. Rev. Lett. **73**, 2484 (1994).

[13] P. J. Hirschfeld *et al.*, Phys. Rev. Lett. **71**, 3705 (1993); S. M. Quinlan *et al.*, Phys. Rev. B **49**, 1470 (1994); P. J. Hirschfeld *et al.*, *ibid*. **50**, 10 250 (1994).

[14] S. J. Hagen, Z. Z. Wang, and N.-P. Ong, Phys. Rev. B **40**, 9389 (1989).

[15] T. T. M. Palstra *et al.*, Phys. Rev. Lett. **64**, 3090 (1990).

[16] M. Sera *et al.*, Solid State Commun. **74**, 951 (1990).

[17] V. Florentiev *et al.*, *Progress in High Temperature Superconductivity,* edited by R. Nicolsky (World Scientific, Singapore, 1990), Vol. 25, p. 462.

[18] S. D. Peacor *et al.*, Phys. Rev. B **44**, 9508 (1991).

[19] J. L. Cohn *et al.*, Physica (Amsterdam) **192C**, 435 (1992).

[20] J. L. Cohn *et al.*, Phys. Rev. B **43**, 13 144 (1992).

[21] R. C. Yu *et al.*, Phys. Rev. Lett. **69**, 1431 (1992).

[22] A. V. Inyushkin, Physica (Amsterdam) **194-196B**, 479 (1994).

[23] Z. Gold *et al.*, Physica (Amsterdam) **235-240C**, 1485 (1994).

[24] P. Henning *et al.*, J. Supercond. **8**, 453, 1995.

[25] J. L. Cohn (unpublished).

[26] M. F. Crommie and A. Zettl, Phys. Rev. B **41**, 10 978 (1990).

[27] N. V. Zavaritsky, A. V. Samoilov, and A. A. Yurgens, Physica (Amsterdam) **169C**, 174 (1990); **185-189C**, 1817 (1991).

[28] F. G. Aliev *et al.*, Solid State Commun. **82**, 241 (1992).

[29] G. Briceno and A. Zettl, Bull. Am. Phys. Soc. **38**, 387 (1993); G. Briceno (private communication).

[30] F. Yu *et al.*, Physica (Amsterdam) **235-240C**, 1489 (1994).

[31] D. T. Morelli *et al.*, Phys. Rev. B **41**, 2520 (1990); D. T. Morelli *et al.* in *High Temperature Superconductors: Fundamental Properties and Novel Materials Processing*, edited by D. K. Christen, J. Narayan, and L. F. Schneemeyer, MRS Symposia Proceedings No. 169 (Materials Research Society, Pittsburgh, 1990), p. 1101.

[32] Y. Nakamura *et al.*, Physica (Amsterdam) **185-189C**, 1409 (1991).

[33] J. L. Tallon and N. E. Flower, Physica (Amsterdam) **204C**, 237 (1993).

[34] J. L. Tallon *et al.*, Phys. Rev. B **51**, 12 911 (1995).

[35] P. J. Ouseph and M. Ray O'Bryan, Phys. Rev. B **40**, 4123 (1990); S. D. Obertelli, J. R. Cooper, and J. L. Tallon, *ibid.* **46**, 14 928 (1992).

[36] M. S. Osofsky *et al.*, Phys. Rev. B **45**, 4916 (1992).

[37] M. E. Parks *et al.*, J. Solid State Chem. **79**, 53 (1989).

[38] J. W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993).

[39] J. L. Tallon *et al.*, Phys. Rev. Lett. **74**, 1008 (1995); J. L. Tallon and J. W. Loram, J. Supercond. **7**, 151 (1994).

[40] D. N. Basov *et al.*, Phys. Rev. Lett. **74**, 598 (1995).

[41] A. Junod *et al.*, Physica (Amsterdam) **162-164C**, 498 (1989).

[42] V. Z. Kresin and S. A. Wolf, Phys. Rev. B **46**, 6458 (1992); S. D. Adrian *et al.*, *ibid.* **51**, 6800 (1995).

[43] C. Popoviciu and J. L. Cohn (unpublished).

[44] For Bi-2212 the mean-field specific heat jump is not well defined [W. Schnelle *et al.*, Physica **209C**, 456 (1993); A. Junod *et al.*, Physica **194-196B**, 1497 (1994)]. For Tl-2201 and LSCO, more κ data are needed.

[45] Thermal resistivities are not additive when scattering is strongly energy dependent.

[46] J. L. Cohn, C. K. Lowe-Ma, and T. A. Vanderah, Phys. Rev. B **52**, R13 134 (1995).

[47] M. Salamon *et al.*, J. Supercond. **8**, 449 (1995).

[48] M. J. Graf, S.-K. Yip, J. A. Sauls, and D. Rainer (unpublished).

[49] D. A. Bonn *et al.*, J. Supercond. **6**, 219 (1993).

[50] H. Claus *et al.*, Physica (Amsterdam) **198C**, 42 (1992); **200C**, 271 (1992); T. Ito *et al.*, Phys. Rev. Lett. **70**, 3995 (1993).

[51] We have subtracted 0.03 from the x values cited in Ref. 49 to bring them into agreement with those inferred from the authors' reported values of T_c and λ.

[52] N. V. Zavaritskii, A. V. Samoilov, and A. A. Yurgens, JETP Lett. **48**, 242 (1988).

[53] J. Bardeen *et al.*, Phys. Rev. **113**, 982 (1959); B. J. Mrstik and D. M. Ginsberg, Phys. Rev. B **5**, 1817 (1972); F. Marsiglio, *ibid.* **44**, 5373 (1991).

[54] O. V. Dolgov *et al.* (private communication).