Low-Temperature Phase Transition in Bi$_2$Sr$_2$Ca(Ni$_x$Cu$_{1-x}$)$_2$O$_8$: Evidence for Unconventional Superconductivity

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(September 4, 1997)

Abstract

We report the discovery of a low-temperature phase transition in Bi$_2$Sr$_2$Ca(Ni$_x$Cu$_{1-x}$)$_2$O$_8$ high temperature superconductor. This transition manifests itself as a sharp reduction of the thermal conductivity of the samples at a temperature $T_c^* \approx 200$ mK. The temperature dependence of the thermal conductivity changes dramatically from $T^\alpha$ with $\alpha$ between 1.6 and 1.75 above the transition to T-linear behavior below the transition. Application of a small magnetic field suppresses the low-temperature phase. We interpret this behavior as a phase transition into a second bulk low-temperature superconducting state in which the time-reversal symmetry is likely to be broken. This discovery constitutes direct evidence for unconventional superconductivity in high temperature superconductors.

PACS number(s) 74.72.Bk, 74.25.Fy, 74.62.Fj

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Unconventional superconductivity is a very active area of research, both in cuprate and heavy-fermion compounds. These two classes of materials hold the possibility that the attractive interaction between charge carriers originates not from the electron-phonon interaction, as in conventional superconductors, but rather from the magnetic fluctuations present in these systems. Such an interaction may result in a superconducting state with the symmetry of the order parameter lower than that of the underlying lattice. These states are called unconventional, as opposed to the s-wave phonon-mediated conventional superconductors. If a particular compound has more than one superconducting phase, at least one of these phases must be unconventional, because there is only one possible symmetry for the s-wave state: that of the underlying crystallographic lattice. Therefore, the presence of multiple superconducting phases is a sufficient but not a necessary condition for an unconventional state. Until recently, only one of the suspected unconventional superconductors - UPt$_3$ [1] - has been unambiguously shown to have more than one superconducting phase. It was first shown that there are two phase transitions out of the zero-field low-temperature superconducting state when magnetic field is increased [2–4]; then two transitions were resolved in zero-field heat capacity measurements [5]; and finally a complete phase diagram was constructed using ultrasound velocity [6]. These results were immediately accepted as proof that superconductivity in UPt$_3$ is unconventional (for a recent review of the heavy-fermion superconductivity, see Ref. [7]). An unambiguous observation of multiple superconducting states in high temperature superconductors would settle the question of whether superconductivity in this class of compounds is indeed unconventional.

In this article we report on the observation of a second low-temperature superconducting phase transition in Ni-doped Bi$_2$Sr$_2$CaCu$_2$O$_{8}$ high temperature superconductor. The low-temperature phase transition manifests itself as a dramatic drop of thermal conductivity between $T_c^* = 200$ mK and 160 mK. Our discovery of multiple superconducting phases in a high temperature superconductor unambiguously answers the question of whether superconductivity in this class of compounds is of unconventional character: it is. There is by now a large body of experimental work on high temperature superconductors that was interpreted
as evidence of unconventional d-wave pairing. It includes observation of a phase shift of $\pi$ in the corner dc SQUID experiments [8], linear-in-temperature microwave penetration depth in the low temperature limit [9], and large gap anisotropy via angle-resolved photoemission [10]. Our results give support to the conclusions about the unconventional character of the high temperature superconductors that were drawn from these measurements.

The Bi-2212 samples used for thermal conductivity measurements were prepared by the traveling solvent floating zone technique [11]. Individual samples were obtained by cutting parts of the rods out and cleaving them down to an appropriate size. The samples used for thermal conductivity measurements were thin rectangular slabs, with thickness varying between 10 $\mu$m and 80 $\mu$m and a surface area of about 1 mm $\times$ 5 mm. The nominal concentrations of Ni dopant substituted for Cu (which was determined by the ratios of the starting materials) varied between 0% and 2.4% for the two series of samples investigated. We characterized the samples by measuring resistance and magnetization. Superconducting transition temperatures were obtained as the intersection points of linear fits to the magnetization curve in the region of its rapid change below the transition and the flat background above the transition. All of the samples used for thermal conductivity measurements had magnetic transition widths of about 1 K, which indicates the high quality and homogeneity of the samples. During the growth of the sample by the traveling solvent floating zone technique, impurities may be redistributed along the sample rod. For example, impurities may be pushed preferentially to the ends of the sample rod. The samples used in this work had the following nominal Ni concentrations and $T_c$’s: 0% Ni - $T_c = 89$ K, 0.6% Ni - $T_c = 78$ K, 1.5% Ni - $T_c = 77$ K, and 2.4% Ni - $T_c = 74$ K. The superconducting transition temperatures reflect the true concentration of the Ni impurities better then the nominal Ni concentrations. Therefore we will identify different samples by their $T_c$’s in the rest of the article.

We used a standard steady state “two heaters, one thermometer” method to collect the thermal conductivity data. One end of the sample is thermally sunk to the bath, and the thermometer is thermally attached to the opposite end. Two resistive heaters are thermally
attached at different points along the sample between the bath and thermometer contacts. By separately turning the heaters on and measuring thermometer’s temperature in both cases one can easily deduce the thermal conductivity of a section of a sample between the two points where the heaters are thermally attached. Silver pads for thermal contacts to bath, heaters and thermometer were evaporated onto the samples and annealed at 300°C for two hours. We used silver paint to attach samples to the bath. Annealed 25 µm-diameter platinum wires provided thermal links from the sample to the thermometer and to the two heaters.

Fig. 1 shows the thermal conductivity data as a function of temperature on a log-log plot for several samples with different nominal Ni concentration. The samples in Fig. 1 are identified by their upper superconducting transition temperatures, which reflect the true level of impurity concentration. The two samples that display phase transitions have $T_c = 77$ K and 78 K. We observed the $T_c^* = 200$ mK transition in the sample with $T_c = 77$ K on three different cooldowns, in two different thermal conductivity cells, with two different sets of platinum thermal leads, and two different thermal connections between the sample and the bath. The low-temperature phase transition therefore is a robust and reproducible property of the sample.

The large size of the drop in thermal conductivity indicates that the transition takes place within the main thermal transport channel of the system. Thermal conductivity $\kappa$ is a sum of two components: $\kappa = \kappa_{el} + \kappa_{ph}$, where $\kappa_{el}$ and $\kappa_{ph}$ are electronic and phonon thermal conductivity. We can make an upper limit estimate the low-temperature phonon thermal conductivity in Bi-2212 by using the expression $\kappa_{ph} = \frac{1}{3} \beta \langle v_{ph} \rangle \Lambda_0 T^3$ [12], similar to the calculation of this limit for YBCO [13]. Here $\beta$ is a coefficient of the $T^3$ (phonon) term of the heat capacity, $\langle v_{ph} \rangle = v_L(2s^2 + 1)/(2s^3 + 1)$, with $s = v_L/v_T$, the ratio of the longitudinal to transverse velocities [12]. For single crystals $\Lambda_0 = 2\pi/\sqrt{\pi}$, where $\pi$ is the geometric mean width of a rectangular sample. Using the tabulated values for longitudinal and transverse sound velocity as well Debye temperature $\Theta_D$ [14] ($\Theta_D$ is used to calculate $\beta$), we estimate the phonon contribution to the thermal conductivity to be 7 times smaller.
in Bi-2212 than in YBCO for samples with the same physical dimensions. Specifically for the 1.5% Ni-doped Bi-2212 sample ($T_c = 77$ K) that shows a second low-temperature phase transition, we calculate the phonon thermal conductivity to be $\kappa_{ph} = 0.2 \times T^3$ W/mK$^4$, or 1.6 mW/Km at $T = 200$ mK. Comparing this number with the experimental value of $\kappa = 9$ mW/Km at $T = 200$ mK, we see that phonon contribution is a small fraction of the total thermal conductivity and cannot account for the drop of about 7 mW/Km between 200 mK and 150 mK. Therefore, the phase transition at $T_c^* = 200$ mK must have an electronic origin.

A slowly opening energy gap that accompanies a second-order superconducting phase transition leads to a smooth decrease of the electronic thermal conductivity as a function of temperature. This is the behavior exhibited by most of the conventional superconductors like Al, Sn, Nb, In, and others. Therefore, the smooth change in thermal conductivity in Fig. 1 is indicative of the second-order character of the low-temperature phase transition. An alternative explanation of rounding of the thermal conductivity data at the phase transition is an inhomogeneous distribution of the Ni impurities. Such an explanation appears unlikely in view of the extremely sharp character of the high temperature superconducting transitions in both of the samples displaying the second low-temperature phase transition.

The data in the high-temperature phase (both for the samples with and without the low-temperature phase) between 50 mK and 2 K can be described very well by a single power law $\kappa = T^\alpha$ with $\alpha$ between 1.6 and 1.75. However, as Fig. 2 shows, the low temperature data can be equally well described as the sum of a linear and quadratic temperature dependence. Indeed, the latter term follows directly from the theory of electronic thermal conductivity of Bardeen, Rickayzen, and Tewordt [15] applied for a pure 2D d-wave superconductor in the limit $T \ll \Delta$ [16]. The $T^2$-dependence is due to the low energy quasiparticle states in the nodes of the $d_{x^2-y^2}$ order parameter.

Below the low-temperature transition the nearly $T^2$-term is quickly suppressed and the thermal conductivity data become linear in temperature. This feature is emphasized in the main body of Fig. 4, which shows thermal conductivity divided by temperature as a function of temperature. In a pure conventional s-wave superconductor with a fully gapped Fermi
surface all of the quasiparticle states are frozen out far below the superconducting transition temperature $T_c$, and all of the thermal transport is due to phonons, with the phonon thermal conductivity $\kappa_{ph} \propto T^3$. As was discussed in the context of conventional low-temperature superconductors, introduction of pair-breaking magnetic impurities leads to the formation of intra-gap impurity states [17] (Shiba states) and impurity bands (for sufficiently large impurity concentration). The impurity band can lead to the formation of tails in the DOS that extend to zero energy [17,18], leading to a nonzero DOS at $E = 0$. If the scattering is strong, the impurity band is close in energy to the mid-gap point and produces a roughly energy-independent DOS. Such a constant DOS in the region about $E = 0$ makes an impurity band metallic in character at low temperature, with the metallic-like thermal conductivity $\kappa/T = \text{constant}$. This is exactly what we observe experimentally, and therefore the thermal conductivity data in the low temperature state is consistent with that of a superconducting state with a fully gapped Fermi surface and an intra-gap impurity band. Opening of the gap eliminates the low-energy nodal quasiparticle states of the $d_{x^2-y^2}$ order parameter that lead to $T^2$ contribution to the thermal conductivity above $T^*_c$. The change in the temperature dependence from nearly quadratic above $T^*_c$ to linear below it reflects the qualitative change of the spectrum of quasiparticle states as the system undergoes the phase transition.

To investigate the nature of the low-temperature transition, we repeated thermal conductivity measurements on a sample with $T_c = 77$ K with a magnetic field of several hundred Gauss applied by placing a small permanent magnet near the sample. The results of this measurement are shown in Fig. 2. The magnetic field suppressed the phase transition. The values extrapolated to $T = 0$ are close to the universal low temperature thermal conductivity limit for doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ [19–21, 13, 22] in a d-wave phase, which is also indicated in Fig 2. However, since the density of states in an impurity band depends on the impurity concentration, we do not expect the thermal conductivity in the low-temperature phase with fully gapped Fermi surface to be universal in the low temperature limit.

The inset of Fig. 2 shows a log-log plot of the thermal conductivity as a function of temperature for one of the samples that underwent the low-temperature phase transition.
The data in field follow a single power law between 50 mK and 2 K as for the samples that did not display the low-temperature phase transition. Detailed quantitative investigation of the effect of the magnetic field is in progress.

All of the features of the data presented in our paper are consistent with a second low-temperature superconducting transition. To summarize: 1) the sharp drop in thermal conductivity indicates the loss of a substantial number of primary heat carriers in the system, i.e. normal quasiparticles; 2) the different temperature dependence above and below the transition implies qualitatively different quasiparticle excitation spectra in the two phases, indicating different order parameters; 3) the linear-in-temperature dependence of the thermal conductivity in the low-temperature phase is consistent with the metallic-like contribution of the impurity band in a fully gapped superconductor; 4) a modest magnetic field appears to suppress the low-temperature phase. Once it is established that the second phase is in fact a different superconducting phase, the rest of the argument follows: superconductivity is unconventional because there can not be two different superconducting states with the same symmetry of the underlying crystallographic lattice in the same compound. Therein lies the significance of our results: one can make a general statement about (un)conventionality of a superconducting state based on the discovery of two different superconducting phases in a compound. The statement is that the superconductivity in such a compound is indeed unconventional. Such a conclusion does not depend on the exact microscopic nature of the first or second superconducting state.

There are several possible scenarios that may be responsible for the low-temperature phase transition. One of them is the s-wave pairing of the quasiparticles in the nodes of the d-wave gap (which does not have to be phonon-mediated). Another is a new phase that is stabilized by interaction of the condensate with magnetic field produced by Ni impurities. The presence of pairbreaking impurities (Ni is most likely a magnetic impurity in Bi-2212 \cite{23,24}) leads to the finite DOS for nodal quasiparticles which in turn can participate in the second phase transition at $T_\ast^c \approx 200$ mK. However, magnetic impurities also act as pair breakers for s-wave superconducting states, whereas nonmagnetic impurities do
not\textsuperscript{25}. Therefore, within the s-wave scenario, increasing the concentration of Ni impurities leads to a competition between an increased DOS that are able to take advantage of pairing and increased pairbreaking and quasiparticle scattering rate. This competition may explain the absence of the low-temperature phase both in the undoped and in the 2.4\%Ni-doped samples (see Fig. 1): the undoped sample does not have a large enough low-energy DOS, and the pairbreaking effect of impurities dominates in the 2.4\% Ni-doped sample, suppressing the second phase.

When the d-wave nodes are gapped at the low-temperature phase transition, which is indicated by the qualitative change in the temperature dependence of the thermal conductivity data, it is likely that the low-temperature state breaks time reversal symmetry. For example, consider going from a d-wave state to a sum of a d-wave and an s-wave order parameters. The nodes of the $d_{x^2-y^2} + s$ order parameter are simply moved to slightly different positions on the Fermi surface (for $|s| \ll |d|$) from their positions for the $d_{x^2-y^2}$ superconducting state. Therefore, to completely gap the nodes of the $d_{x^2-y^2}$ order parameter, the s-wave component must be added with a different phase (as an imaginary part), i.e. the low-temperature (complex) order parameter must have a $d + is$ symmetry to allow for a non-zero gap value everywhere on the Fermi surface. The same is true for an order parameter that is the sum of two different d-wave components, $d_{x^2-y^2}$ and $d_{xy}$. Such a state must have a $d + id$ symmetry to have a non-zero gap value everywhere on the Fermi surface. Such a complex order parameter leads to broken time reversal symmetry, an exciting possibility that should be reflected in a number of unusual physical properties. Spontaneous orbital currents in such states were considered originally by Anderson and Morel\textsuperscript{26}. More recently the signatures of broken time reversal symmetry were investigated in heavy fermions\textsuperscript{27,28}, where models that describe most of the experimental observations in superconducting UPt$_3$ lead to spontaneous orbital moments of the Cooper pairs.

Thermal conductivity is a bulk probe. We therefore conclude that the phase transition we observe is an intrinsic bulk property of the Ni-doped Bi-2212. For that reason, this low-temperature transition is different from the recently reported anomalies in tunneling into
YBa$_2$Cu$_3$O$_7$[29], which can be understood in terms of the appearance of the subdominant order parameter at the surface of the high temperature superconductor. Surface-induced states that violate time-reversal symmetry were discussed originally by Sigrist et al. [30].

Generation of the secondary order parameter due to Andreev bound states on the surface has been recently discussed by Sauls and co-workers [31], who also considered broken time-reversal symmetry for the case of such surface-induced states in d-wave superconductors.

Recently, K. Krishana et al. reported an observation of an anomaly in the thermal conductivity data as a function of magnetic field in single crystals of pure Bi$_2$Sr$_2$CaCu$_2$O$_8$[16]. They observe a sharp change in the slope of the thermal conductivity with magnetic field (field sweeps were performed at constant temperature ranging from 6 K to 20 K). Thermal conductivity first decreases by a few percent with increasing magnetic field up to a critical field $H_c$ of several Tesla, and then becomes field-independent. This anomaly may be a consequence of the transition into a $d + id$ state [32]. If the low-temperature state in Ni-doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ is driven by the interaction between the magnetic field produced by the Ni-impurities and the condensate, both of these phenomena might be related.

The low-temperature phase transition at $T^*_{c} \approx 200$ mK must be accompanied by a feature in specific heat. We performed specific heat measurements on 1%Ni- and 2%Ni-doped Bi-2212 samples grown by a self-flux technique [33], which produced shiny, micaceous samples with a typical surface area of 10 mm$^2$. We used a semi-adiabatic heat pulse method to collect the specific heat data. We do not see any feature in the data around 200 mK that would indicate a phase transition. A smooth background results from a nuclear Schottky feature and a linear-in-temperature term, similar to the data for pure Bi-2212 [34]. At 200 mK $C \approx 20$ mJ/mol K, which is about two orders of magnitude greater than specific heat values at this temperature for typical metals. Given our null results, the size of the feature in specific heat at the low-temperature transition is less then 0.2 mJ/molK (precision of our measurement is $\approx 1\%$). This makes observation of the low-temperature phase transition via specific heat measurement a very challenging experiment, and also highlights the utility of thermal conductivity measurements as a probe of this transition.
In conclusion, we have discovered a low-temperature phase transition at $T^{*}_c = 200\,\text{mK}$ in the high temperature superconductor $\text{Bi}_2\text{Sr}_2\text{Ca(}\text{Ni}_x\text{Cu}_{1-x}\text{)}_2\text{O}_8$. The phase transition manifests itself as a sharp drop in the thermal conductivity between $T^{*}_c \approx 200\,\text{mK}$ and $160\,\text{mK}$. This phase is suppressed by the application of a weak magnetic field. We interpret our observations as evidence for a second low-temperature superconducting phase in $\text{Bi}_2\text{Sr}_2\text{Ca(}\text{Ni}_x\text{Cu}_{1-x}\text{)}_2\text{O}_8$. Such observation of multiple superconducting phases in high temperature superconducting compounds is a manifestation of the unconventional character of superconductivity in these materials. This low-temperature superconducting state probably breaks time-reversal symmetry.

Acknowledgements: We thank R. Ecke for his help with the data acquisition hardware and for his invaluable assistance with the manuscript. We thank H. Safar for his help with sample preparation. We are grateful to J. D. Thompson and J. L. Smith for useful discussions. We thank J. A. Sauls, L. Taillefer, and N. P. Ong for making available the preprints of their articles prior to publication. D. Hristova helped with the operation of the cryogenic apparatus. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy. M. A. Hubbard and M. B. Salamon acknowledge support by the National Science Foundation (DMR 91-20000) through the Science and Technology Center for Superconductivity.
REFERENCES

[1] G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. 52, 679 (1984).

[2] Y. J. Qian et al., Solid State Commun. 63, 599 (1987).

[3] V. Müller et al., Phys. Rev. Lett. 58, 1224 (1987).

[4] A. Schenstrom et al., Phys. Rev. Lett. 62, 332 (1989).

[5] R. A. Fisher et al., Phys. Rev. Lett. 62, 1411 (1989).

[6] S. Adenwalla et al., Phys. Rev. Lett. 65, 2298 (1990).

[7] R. H. Heffner and M. Norman, Comments in Cond. Mat. Phys. 17, 361 (1996).

[8] D. A. Wollman et al., Phys. Rev. Lett. 71, 2134 (1993).

[9] W. N. Hardy et al., Phys. Rev. Lett. 70, 3999 (1993).

[10] Z. X. Shen et al., Phys. Rev. Lett. 70, 1553 (1993).

[11] R. Yoshizaki, I. Tomitsuka, K. Ueno, and H. Ikeda, J. Low Temp. Phys. 105, 927 (1996).

[12] P. D. Thacher, Phys. Rev 156, 975 (1967).

[13] L. Taillefer et al., preprint.

[14] J. Dominec, Supercond. Sci. Technol. 6, 153.

[15] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. 113, 982 (1959).

[16] K. Krishana et al., preprint.

[17] L. Yu, Acta Physica Sinica 21, 75 (1965); H. Shiba, Prog. Theor. Phys. 40, 435 (1968); A. I. Rusinov, Sov. Phys. JETP Lett. 9, 85 (1969). See also M. I. Salkola et al., Phys. Rev. B, May 1 (1997), M. Flatte and J. Byers, Phys. Rev. Lett., to be published, 1997.

[18] A. V. Balatsky and S. Trugman, to be published.
[19] P. Herschfeld et al., Solid State Commun. 59, 111 (1986).

[20] S. Smitt-Rink et al., Phys. Rev. Lett. 57, 2575 (1986).

[21] M. J. Graf, S.-K. Yip, J. A. Sauls, and D. Rainer, Phys. Rev. B 53, 15147 (1996).

[22] detailed comparison of the data Ni-doped Bi-2212 with theoretical predictions for universal low-temperature conductivity will be presented elsewhere.

[23] K. Ishida et al., Journ. of Phys. Soc. Japan 62, 2803 (1993).

[24] Y. Kitaoka et al., J. Phys. and Chem. of Solids 54, 1385 (1993).

[25] P. W. Anderson, Phys. Rev. Lett. 3, 325 (1959).

[26] P. W. Anderson and P. Morel, Phys. Rev. 123, 1911 (1961).

[27] M. Sigrist and K. Ueda, Rev. Mod. Phys. 63, 239 (1991).

[28] J. Sauls, Adv. Phys. 43, 113 (1994).

[29] M. Covington et al., preprint.

[30] M. Sigrist, D. Bailey, and R. Laughlin, Phys. Rev. Lett. 74, 3249 (1995).

[31] M. Fogelström, D. Rainer, and J. A. Sauls, preprint, 1997; M. Palumbo, L. J. Buchholtz, D. Rainer, and J. A. Sauls, preprint, 1997.

[32] R. Laughlin, private communication.

[33] C. Kendziora et al., Phys. Rev. B 45, 13025 (1992).

[34] J. Baak et al., Physica C 210, 391 (1993).
FIG. 1. Thermal conductivity of several Ni-doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ samples. - undoped, T$_c$ = 89K; ◆ - T$_c$ = 78K; • - T$_c$ = 77K; △ - T$_c$ = 74K.

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Fig. 2. Thermal conductivity divided by temperature as a function of temperature.

- undoped, $T_c = 89 \text{K}$;
- $\Delta - T_c = 74 \text{K}$;
- $\bullet - T_c = 77 \text{K}$, $H = 0$;
- $\bigtriangledown - T_c = 77 \text{K}$, $H \approx 200 - 300 \text{G}$.

Inset: thermal conductivity of Bi$_2$Sr$_2$CaCu$_2$O$_8$ sample with $T_c = 90 \text{K}$.