Title
Electrodynamics of single-crystal Eu2CuO4 — A boson excitation spectrum

Journal
Synthetic Metals, 29(2-3)

ISSN
0379-6779

Authors
Reagor, DW
Cheong, S
Brown, SE
et al.

Publication Date
1989-03-01

DOI
10.1016/0379-6779(89)90966-1

Synthetic Metals, 29 (1989) F657–F666

ELECTRODYNAMICS OF SINGLE-CRYSTAL Eu_2CuO_4 – A BOSON EXCITATION SPECTRUM

D.W. REAGOR, S. CHEONG, S. E. BROWN, A. MIGLIORI, Z. FISK and J. D. THOMPSON
Los Alamos National Laboratory, P-10, MS K764, Los Alamos, NM 87545 (U.S.A.)

ABSTRACT

Static and microwave measurements of the electronic response of the planar cuprate Eu_2CuO_4 provide evidence for thermally activated collective excitations. These observations together with microwave and other measurements on superconductors suggest that paired charge-carrying objects may exist both above and below T_c in the superconductors. If these objects, which can be related to solitons of a spin density wave ground state, play a role in superconductivity, certain conclusions may be drawn. We discuss here the evidence for such objects and their implications.

The availability of single-crystal intrinsic semiconductors of the so-called 214 planar cuprates makes precision microwave measurements attractive because of the low conductivity of these materials. Though the materials are not metallic and display some form of magnetic ordering, the few carriers present may provide a model for the behavior in the non-magnetic metallic (superconducting) state.

Superconductivity is a collective[1] transport arising from a highly-correlated ground state. The electrodynamic response consists of an undamped collective mode at zero frequency. Other electronic collective modes arise from charge density or spin density wave ground states and are present in the microwave spectral range.[2] Thus microwave measurements can provide useful information about collective transport in highly correlated electronic systems. In this work we describe our measurements of a unique collective mode in the insulating ground state of Eu_2CuO_4 and connect them with observations by others to present a picture in which charged, spinless collective excitations could play a role in superconductivity.

0379-6779/89/$3.50

Eu_2CuO_4 has been grown as large single crystal plates (0.3 cm^2 x 0.005 cm) from a PbO flux. The a axes are in the plane of the plates. X-ray diffraction measurements indicate a single phase with lattice constants a = 3.91 Å, c = 11.93Å. It is characterized by an optical gap[3] which, in light of the predicted half-filled band, must arise from electron-electron interactions, and by an activated dc conductivity with activation energy an order of magnitude lower than the gap. Weak features in the resistivity near 240 K are observed[4] and from susceptibility measurements are interpreted as indicating a Neel temperature (T_N). Hall measurements[4] on samples from the same batch yield a carrier density $n = 10^{18}/cm^3$ at 300 K with an activation energy of 700 K. We found our samples to have a resistivity of 3 Ω-cm at 300 K as shown in Fig. 1 with an activation energy of 1310 K over the temperature range of 80 K to 300 K implying an activated mobility.

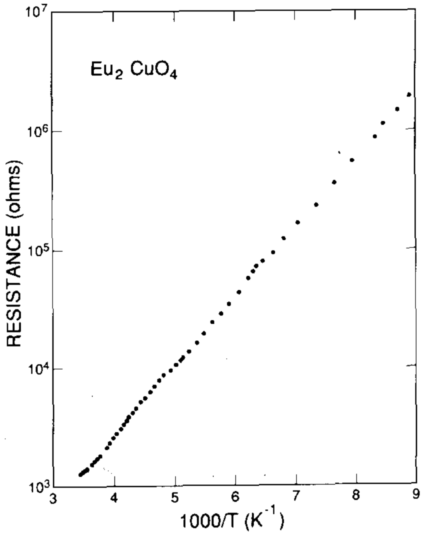

Fig. 1 Four probe dc resistance of Eu_2CuO_4 single-crystal. The solid line is $R = R_o \exp(-T_o/T)$ with T_o = 1310 K.

The optical spectrum is remarkably clean with an IR-active carrier density[3] $n \lesssim 10^{18}/cm^3$. Such a low IR-carrier density leaves the origin of dc conductivity in question because carrier sources such as impurity levels would require 10^{19} impurity sites. Another oxide superconductor $BaPb_{1-x}Bi_xO_3$ has the same spectroscopic anomaly, dc conduction with an activation energy much lower than the gap and insufficient extrinsic carrier sources.[5] We will discuss below a mechanism for this unusual transport.

The planar cuprates La_2CuO_4, Eu_2CuO_4 and oxygen deficient $RE_1Ba_2Cu_3O_{7-x}$ (x > 0.5) all share an optical gap[3] of ~1.7 eV and magnetic transitions[4] near 240 K indicating identical intrinsic excitations. The observation of superconductivity at 95 K in many compounds with Cu-O planes also confirms that the Cu-O planes play an important role. The Eu_2CuO_4 compound differs[4] from the La_2CuO_4 analog[6] in that it is tetragonal rather than orthorhombic and its out-of-plane oxygens are in another location. In addition, Eu_2CuO_4 has a much lower conductivity because of a lower impurity concentration, revealing intrinsic processes obscured in La_2CuO_4.

Microwave conductivity measurements were made using a unique coaxial microwave bridge. This technique for waveguide bridges is described elsewhere.[7] Our method differs only in that it is implemented in coaxial line and is therefore tunable over a full decade, from 2 GHz to 20 GHz. The samples to be measured were mounted directly across one open coaxial arm of the bridge.

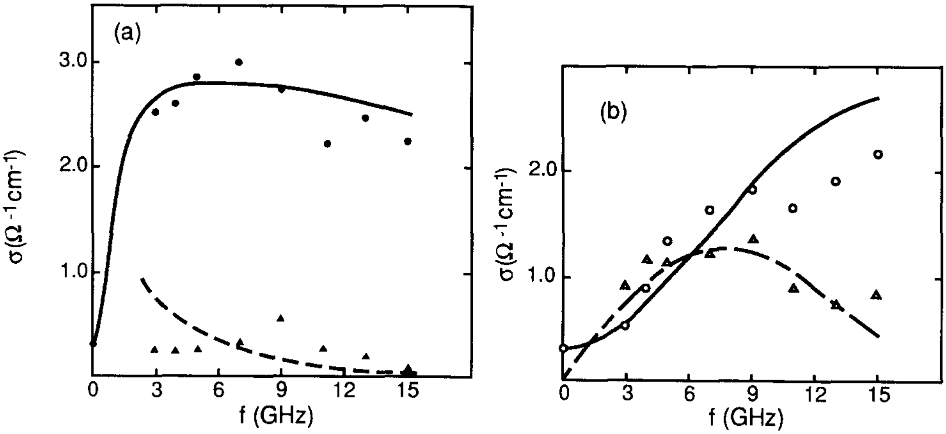

Fig. 2 Frequency dependent complex conductivity for two single-crystal samples of Eu_2CuO_4. a) sample #1, b) sample #2, O, real conductivity, Δ, imaginary conductivity. The fits are to Eq. 1, solid lines Re(σ), dashed lines Im(σ).

The microwave complex conductivity of Eu_2CuO_4 at 300 K is displayed in Fig. 2 for two samples. The peak imaginary conductivity of both samples is much lower than the real part, indicating a resonance. For a simple harmonic oscillator the peak imaginary conductivity is half the peak real conductivity. Thus, the curves in Fig. 2 which are fits to a harmonic oscillator model,[2] correspond to the same oscillator strength for both samples, where

$$\sigma = \sigma_{dc} + \frac{ne^2\tau}{m^*}\,\frac{i\omega}{i\omega + (\omega_o^2 - \omega^2)\,\tau} + \frac{i\omega\epsilon_\infty}{4\pi} \tag{1}$$

and the fit parameters are $ne^2\tau/m^* = 2.5\ (\Omega - \mathrm{cm})^{-1}$, $\sigma_{dc} = 0.3\ (\Omega - \mathrm{cm})^{-1}$, $1/2\pi\tau = 35$ GHz in all cases. The mode frequency, ω_o, is 6 GHz and the infinite frequency dielectric constant, ϵ_∞, is 100 for sample #1; ω_o is 18 GHz and ϵ_∞ is neglected for sample #2. The fits to $\sigma(\omega)$ with Eq. 1 are in good agreement with the experimental results, except for Im σ of sample #1. Such an effect is difficult to avoid when Re σ is much larger than Im σ. The slightly different values of ϵ_∞ for the two samples would then be an artifact. The spectral weight of the resonance is strongly temperature dependent so that by 150 K the peak conductivity is only $0.5\ (\Omega - \mathrm{cm})^{-1}$. We note that the temperature dependence of the resonant frequency and width is weak and not detectable, a quality observed in CDW and SDW systems where the frequency is determined only by the defect density, which provides pinning sites for microwave conduction and a hopping mobility for dc, just as for our samples here. The different pinning frequencies for the two samples may be due to different impurity concentrations. In CDWs, the resonance width is also observed to be temperature independent, but the mechanism for this is not understood. The temperature dependence of the peak real conductivity, $\sigma_{dc} + ne^2\tau/m^*$ (proportional to spectral weight) is displayed in Fig. 3. From this plot we obtain an activation energy of 630 K,

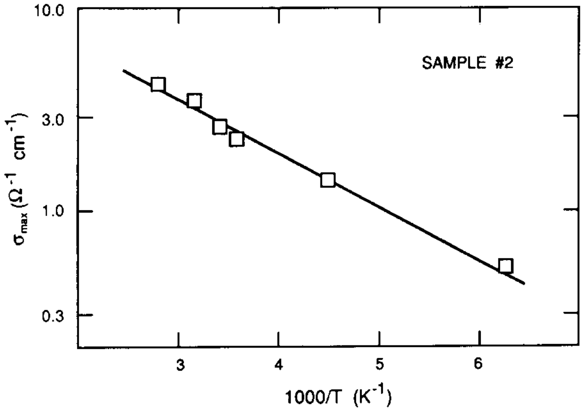

Fig. 3 The peak real conductivity derived from fits to Eq. 1 versus 1000/T. The solid line is a fit to $\exp(-T_o/T)$, with $T_o = 630$ K.

about the same as for the Hall carriers. The effective mass m* of the mode may be estimated from our 300 K microwave data and from the Hall carrier density because of the apparent thermal correspondence between the Hall and microwave carriers. Note that the microwave electric fields are not sufficient to cause hopping, thus we expect the Hall and microwave activation energies to agree. Using σ_{dc}, $ne^2\tau/m^*$, τ and n, we find $m^* \approx 500\ m_e$. The mass estimate is only reliable at an order of magnitude level due to the use of a hall carrier density and an imprecise measurement of τ.

We note that the dc dielectric constant of Eu_2CuO_4 deduced from Fig. 2 is of order 10^3 at 300 K, insuring complete screening of coulomb interactions. Such effects may also be present at low temperatures in the doped material as we discuss below.

A frequency dependent microwave conductivity may result from a number of phenomena. Most mechanisms can be rejected on the basis of frequency, relaxation time or temperature dependence.[8] In contrast, the coherence in modes derived from electronic collective states results in scattering times and pinning frequencies of order 20 GHz for CDWs and SDWs (comparable to our result) and zero for both quantities in superconductors. We see a temperature dependent peak conductivity inconsistent with that of a CDW[9] where far below T_c the spectral weight saturates. In a one-dimensional commensurate SDW Horovitz[10] has shown that charged, spinless solitons are the lowest charged excitations above the ground state. Our system is quasi-two-dimensional. Fermi surface nesting, however, may imply that the cuprates have quasi-one-dimensional characteristics. The mode appears both above and below T_N, therefore the long range order is not important. The lack of long range order ensures that localized states are responsible for the microwave conduction, even though the ground state is not well understood.

Our data place an important constraint on the ground state because we see charged excitations at energies 25 times lower than the 1.7 eV single-electron gap. Such excitations are not possible in a Mott-Hubbard system, with on-site repulsions much larger than transfer energies, where all the low-energy excitations are spin waves. Instead, we require substantial itinerant character leading, qualitatively, to "holes" spread over an area of approximately 25 lattice sites with a creation energy estimated to be $B = 1.7/25\ eV \sim 800\ K$. The itinerant character is also clearly displayed in NMR studies[11] of La_2CuO_4, where the temperature dependence of the sublattice magnetization is <u>not</u> consistent with a local moment ordering.

We propose that the 630 K activation energy indicates that localized states are thermally excited as a positive-negative pair (because the total localized-state charge must be conserved up to single-electron excitation energies of 1.7 eV) from a ground state much like a commensurate SDW but with shorter-range order. The microwave response results from translation of the localized states, which have a metal-like mobility. The dc conduction arises from the same carriers, but with a much lower hopping mobility, explaining the anomalous dc properties. In the superconductors, if a similar ground state existed, such localized states, the lowest charged excitations, could also form through doping of the Cu-O planes with positive charges. The charged, perhaps spinless, localized states would then exist in the ground state of the doped material at T = 0 K. Observations[12] of similar collective modes in the $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ superconductors support this. We note that the excitations in the antiferromagnetic insulator have the same energy as those which break-up order in the superconductor, implying they are closely related.

Thus the possibility that the superconductivity results from superfluidity of the localized states must be examined. To make the connection. assume that the lowest excitation of the localized state is simple translation, the next excitation is destruction of the localized state. The 630-K activation energy in the intrinsic material (equal to $7kT_c$ for the high temperature superconductor) is taken as the binding energy B of the localized state in the doped material. The minimum diameter of the localized state ξ is determined from the spatial extent of an electron in a narrow well, $\xi = 2\hbar/(2\ m_e B)^{1/2} = 16$ Å. The validity of the assumption is supported by the following comparison to other experiments.

Studies of ^{4}He films on flat substrates of porous bulk materials have shown that interactions with the host material result in a minimum coverage of approximately a ^{4}He monolayer, above which superfluidity occurs.[13] In $La_{2-x}Sr_xCuO_4$, T_c remains zero with increasing Sr concentration until $x \cong 0.05$, when superconductivity occurs.[14] In analogy with the ^{4}He we use the minimum density of holes for superconductivity, $0.05((3.9\ \text{Å})^{-2})$ to determine the boson diameter, $\xi = 25$ Å with charge 2e. This is in excellent agreement with the coherence length $\xi = 24$ Å deduced from critical field measurements[15] and with the minimum size $\xi = 16$ Å deduced above from our proposed binding energy. The correspondence is most clearly seen in Fig. 4 where T_c vs. number density of holes is plotted for several high T_c superconductors. The inset is T_c vs. thickness of He^4 films on a flat substrate. The lower T_c data points in Fig. 4 are $La_{2-x}Sr_xCuO_4$ results from Ref. 14. The $YBa_2Cu_3O_x$ results in Ref. 16 are the two higher T_c points. In Ref. 16 it was shown that the T_c plateaus at ≈ 58 for

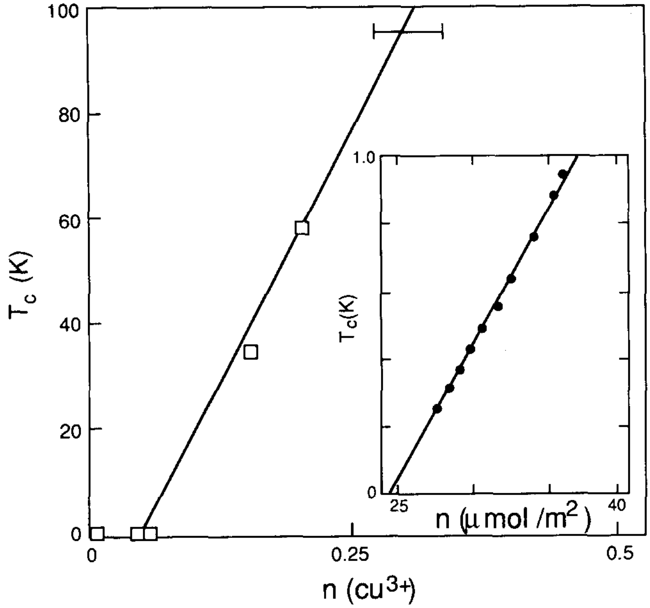

Fig. 4 The T_c of various high temperature superconductors versus carrier density. The results are from Ref. 13, Ref. 14, Ref. 16 and charge count arguments in the text.

x = 6.6 to 6.8. We take the higher value of x since a mixed phase sample will reflect the higher T_c. The T_c of 95 K is obtained over a range x = 6.9 to x = 7.0.

We now compare the properties of this type of superconductivity to several experiments on copper-oxide superconductors, including surface resistance, penetration depth and Raman scattering. The power laws (in temperature or energy) observed in each of these measurements indicate a spectrum that is not gapped. Furthermore, all of the results can be explained in a self-consistent picture that assumes only that the bosons are charged and that they are confined to the Cu-O planes (quasi-two dimensional). The inter-plane coupling is not required to describe the low energy spectrum, but may be necessary to describe the actual phase transition.

We propose that screening of the coulomb interaction leads to a dispersion law

$$E(k) = \hbar C'k \tag{2}$$

at small wave vectors. Here k is the wavevector and C' is the dispersion velocity. This spectrum is exactly what is found in CDW systems except that the high temperature superconductors have a gapless undamped translational mode.[2]

For excitations described by Eq. 2 in two dimensions the density of states is linear in energy up to a cut-off in the linear dispersion at π/a. At low temperatures excitations requiring a minimum energy such as pair-breaking or vortex rings are frozen out in an activated fashion and the density of excitations in the linear portion of the dispersion is

$$n_e = \frac{\pi}{12}\left\{\frac{k_B T}{\hbar C'}\right\}^2 \qquad (3)$$

The dielectric function ϵ of a superconductor in a two fluid model is given by $\epsilon = -Q/\omega^2 + 4\pi n_e\mu/i\omega$, where the first term is the collective mode screening and the second is the loss due to quasiparticles (excited states). Below $T_c/2$ the collective mode is dominant and the surface resistance is approximately

$$R_s = (2\pi/c)\ 4\pi n_e\mu\omega^2/Q^{3/2} \qquad (4)$$

At low temperatures $Q/4\pi$, the collective mode amplitude, depends only on the order parameter and is assumed to be saturated. In a high T_c superconductor, the mobility of the superfluid excitations μ is impurity limited and is therefore temperature independent. It follows that the surface resistance obtains its temperature dependence from the excitation density and both are proportional to T^2.

The surface resistance measurements by Carini et al.[17] in Fig. 5 were performed at 102 GHz and 148 GHz on a c-axis oriented film (electric field in

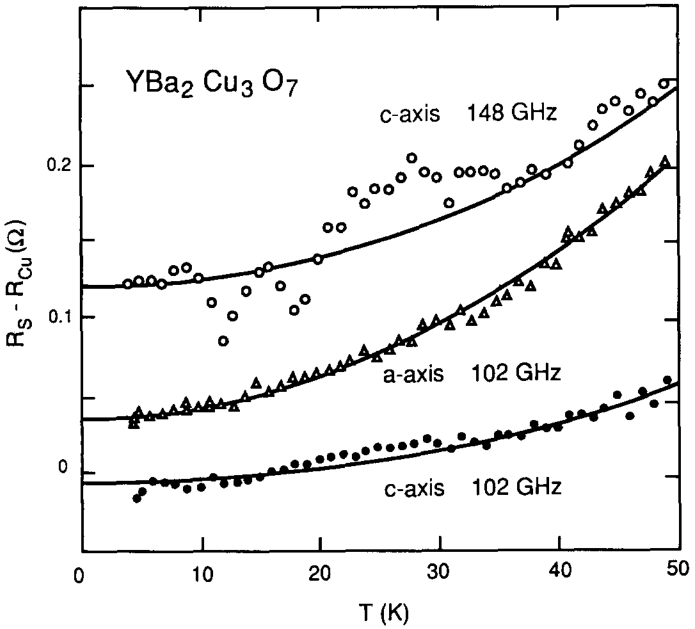

Fig. 5 Surface resistance of $YBa_2Cu_3O_7$ with fits to Eq. 5. The results are reproduced from Carini et al.[17]

the a-b plane), and at 102 GHz on an a-axis oriented film. We have fit the data at 102 GHz to the form

$$R_s = A + B\,T^2\omega^2 \tag{5}$$

for each of the films. The constant A is expected to be a residual term which is not intrinsic. The a-axis film shows clear agreement with the T^2 law, as noted by Carini et al. We also point out that the c-axis measurements are consistent with Eq. 5, although other fits are possible.[17] The 148 GHz fit was produced by scaling the constant B from the 102 GHz fit by ω^2 and using A as the only fit parameter and is also consistent with our model.

The observation of a power law temperature dependence is at odds with that of a BCS superconductor. In the two fluid model the penetration depth is given by $\lambda = c/Q^{1/2}$ where Q is proportional to the condensate density n_c ($n_c = n_o - n_e$). Expanding for n_e small compared to n_o we have

$$\lambda \simeq \lambda_o \left(1 + \frac{n_e}{2n_o}\right) \tag{6}$$

The experiments of J. R. Cooper et al.[18] have shown that $\lambda(T)/\lambda(T = 0) \simeq 1 + T^2/T_o^{\,2}$ with $T_o \simeq 118$ K. Using this result alone we see that a simple boiling-off of the condensate without changing the dispersion exhausts the condensate ($n_e \simeq n_o$) at a temperature $T_c \simeq 100$ K.

The two results above allow us to determine all the parameters of our model (Eq. 2). Using the carrier density calculated from the band filling of the 95 K material, $n_o = 0.33/(3.9 \times 10^{-8})^2$, and the dispersion velocity $\hbar C' = 2.5 \times 10^{-2}$eV - Å. Extrapolating to the zone boundary at $k = \pi/3.9$ Å we have $E(\pi/a) \simeq .02$eV $\simeq 233$ K. This intercept is in agreement with the analysis of the Raman results below.

Studies of the Raman spectra[19] of single crystal $YBa_2Cu_3O_7$ display additional evidence for this excitation spectrum. The Raman spectrum at low temperatures (3 K) consists of phonon lines and a background intensity which increases linearly in energy from the lowest wavevector (16 cm^{-1}) to $\simeq$ 400 cm^{-1}, with a broad maximum at $\simeq$ 500 cm^{-1}. The T = 3 K results are nearly the zero temperature spectrum. At zero temperature the Raman intensity for scattering from pairs of bose excitations is proportional to the density of states for single excitations (the pairs are necessary to conserve crystal momentum). The density of states in the observed Raman intensity increases linearly in energy, in our model above. Furthermore the peak at 500 cm^{-1} corresponds to two excitations of order 350 K, in fair agreement with the energy obtained from extrapolating the dispersion obtained from the penetration depth and millimeter-wave loss measurements.

The results above indicate that massive collective transport is present in the semiconducting (214) copper oxide compounds. The existence of a quasi-two-dimensional charged superfluid in the high temperature superconductors is then conjectured. The conjecture leads to a description of the Raman spectrum, the millimeter-wave loss and the penetration depth measurements in the 95 K superconductor. This work was supported by the U.S. Department of Energy.

REFERENCES

1 M. Tinkham, Introduction to Superconductivity, (McGraw-Hill, New York, 1975).

2 For a review, see G. Gruner and A. Zettl, Phys. Rep. 119 (1985) 117, and articles in Charge Density Waves in Solids, Lecture Notes in Physics, 217 eds. G. Hutiray and J. Sólyom (Springer-Verlag, Berlin, 1986).

3 J. Orenstein, private communication.

4 S-W. Cheong and J. D. Thompson, private communication.

5 S. Uchida, K. Kitazawa and S. Tanka, Phase Trans., 8, (1987) 95.

6 S-W. Cheong, Z. Fisk, J. D. Thompson, J. P. Remeika and G. Gruner, preprint.

7 S. Sridhar, D. Reagor and G. Gruner, Rev. Sci. Instrum., 56 (1985) 1946.

8 D. W. Reagor, A. Migliori, Z. Fisk, et al., PRB.

9 D. Reagor, S. Sridhar and G. Gruner, Phys. Rev. B 34, (1986) 2212; S. Sridhar, D. Reagor and G. Gruner, Phys. Rev. B 34 (1986) 2223 and references cited therein.

10 Baruch Horovitz, in Modern Problems in Condensed Matter Sciences-Solitons, 17 (North-Holland, New York, 1986) 691.

11 H. Nishihara, H. Yasuoka, T. Shimizu, T. Tsuda, T. Imai, S. Sasaki, S. Kanbe, K. Kishio, K. Kitazawa and K. Fueki, submitted to J. Phys. Soc. Jpn.

12 A. S. Shcherbakov, M. I. Katsnel'son, A. V. Trefilov, N. L. Sorokin, E. G. Valiulin and A. N. Petrov, Pis'ma Zh. Eksp. Teor. Fiz., 46 (1987) 111 [JETP Lett., 46 (1987) 136].

13 J. H. Scholtz, E. O. McLean and I. Rudnick, Phys. Rev. Lett., 32 (1974) 147; B. C. Crooker, B. Hebral, E. N. Smith, Y. Takano and J. D. Reppy, Phys. Rev. Lett., 51 (1983) 666.

14 M. W. Schafer, T. Penney and B. L. Olson in Novel Superconductivity (Phenum, New York, 1987) 771.

15 Y. Iye, T. Tamegai, H. Takeya and H. Takei, Physica, 148B (1987) 224.

16 R. S. Kwok, S-W. Cheong, J. D. Thompson, Z. Fisk, J. L. Smith and J. O. Willis, submitted to Physica C.

17 J. P. Carini, A. M. Awasthi, W. Beyermann, G. Gruner, T. Hylton, K. Char, M. R. Beasley and A. Kapitulnik, submitted to Phys. Rev. B, Rapid Commun.

18 J. R. Cooper, C. T. Chu, L. W. Zhou, B. Dunn and G. Gruner, Phys. Rev. B, 37 (1988) 638.

19 S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice and D. M. Ginsberg, submitted to Phys. Rev. B, Rapid Commun.