Evidence for line nodes in the energy gap for $(La_{1.85}Sr_{0.15})CuO_4$ from low-temperature specific-heat measurements

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(Received 26 July 1999; revised manuscript received 27 August 1999)

The dependence of the low-temperature specific heat of $(La_{1.85}Sr_{0.15})CuO_4$ on magnetic field (H) is reported. Low concentrations of paramagnetic centers allow a different approach to analysis of the data that minimizes the problem of identifying the effects of the line nodes in the energy gap that are expected for d-wave pairing. As a consequence, these effects can be recognized even in the raw data. The data show evidence of the T^2 term expected for $H=0$, and a well defined $H^{1/2}T$ term for $H\neq 0$. They conform to a scaling relation recently predicted for d-wave pairing.

Tunneling and vortex-imaging experiments that give information on the symmetry of the order parameter have been interpreted as showing the presence of a dominant d-wave component in $YBa_2Cu_3O_{7-\delta}$ (YBCO).[1] Evidence bearing on the symmetry of the order parameter that might be found in bulk properties is of considerable interest for comparison with these results. The line nodes in the energy gap that are associated with d-wave pairing have substantial effects on the specific heat (C), making it the ideal bulk property for study. There have been several reports of the observation of these effects in YBCO (Refs. 2–5) but there are significant discrepancies among them, which arise, at least in part, from the presence of paramagnetic centers (PC's) and the complication in dealing with their contribution (C_{mag}) to C. In this context, specific-heat measurements on $(La_{2-x}Sr_x)CuO_4$ (LSCO) are of special interest: for comparison with the conflicting results for YBCO; as an extension of such measurements to a cuprate superconductor for which relatively little other evidence on the symmetry of the energy gap is available; and also because the concentration of PC's can be relatively low,[3] making a more definitive determination of the d-wave effects possible.

In the presence of line nodes in the energy gap the contribution (C_{DOS}) of the electron density of states (DOS) to C is expected to have different dependencies on temperature (T) and magnetic field (H) depending on the value of the parameter $z\equiv H^{-1/2}T$ relative to a critical value $z_c \sim H_{c2}^{-1/2}T_c$: For $z<z_c$, i.e., low T and $H\neq 0$, an $H^{1/2}T$ dependence is predicted,[6,7] $C_{\mathrm{DOS}}=\beta H^{1/2}T$. In the widely used notation $C_{\mathrm{DOS}}=[\gamma^*(H)-\gamma^*(0)]T$, where $\gamma^*(0)T$ is the ubiquitous zero-field T-proportional ("linear") term, this corresponds to $[\gamma^*(H)-\gamma^*(0)]=\beta H^{1/2}$. For $z>z_c$, both H-proportional, T-independent and T^2, H-independent terms are predicted,[8] with only the T^2 term, αT^2, occurring for $H=0$.[8,9] These predictions are all consistent with a scaling relation,[10] which is based on general considerations of the quasiparticle excitation spectrum and given in terms of an undetermined function $F(z)$, and which can be written in two forms:

$$C_{\mathrm{DOS}}/H^{1/2}T=F(z), \tag{1}$$

$$C_{\mathrm{DOS}}/T^2=F(z)/z. \tag{2}$$

For YBCO the T^2 and $H^{1/2}T$ terms were first identified in experimental data in a Stanford/UBC Collaboration [2]; LBNL data showed a similar $H^{1/2}T$ term but the validity of the T^2 term was questioned [3]; later LBNL data on better samples, and analyzed with a more accurate expression for C_{mag}, were interpreted as confirming the presence of both terms.[5] The analysis of the data to obtain the T^2 and $H^{1/2}T$ terms was, in each case, complicated by the presence of a significant contribution from the PC's. That complication was avoided by the Geneva group by taking the difference between $C(H)$ measured with H parallel and perpendicular to the c axis.[4] With the assumptions that the DOS contributions scale by a constant factor and all other contributions to $C(H)$ cancel, the difference is proportional to $C_{\mathrm{DOS}}(H)$. However, in essentially the same region of H and T in which the Stanford/UBC and LBNL data show an $H^{1/2}T$ dependence,[2,3,5] the Geneva data show substantially different behavior.[4] The origin of the discrepancy may lie in the assumption of the scaling by a constant factor of C_{DOS} for the two field directions.[12]

We report here measurements on two samples of LSCO, $x=0.15$, that were prepared in different laboratories. The concentrations of PC's are substantially lower than in the YBCO samples mentioned above, and their contributions to the specific heat correspondingly smaller. The predicted d-wave effects can be recognized qualitatively even in the raw data; the $H^{1/2}T$ term is well established; a nonzero $C_{\mathrm{DOS}}(0)$ is clearly present, but its small size precludes a precise determination of its temperature dependence. Al-

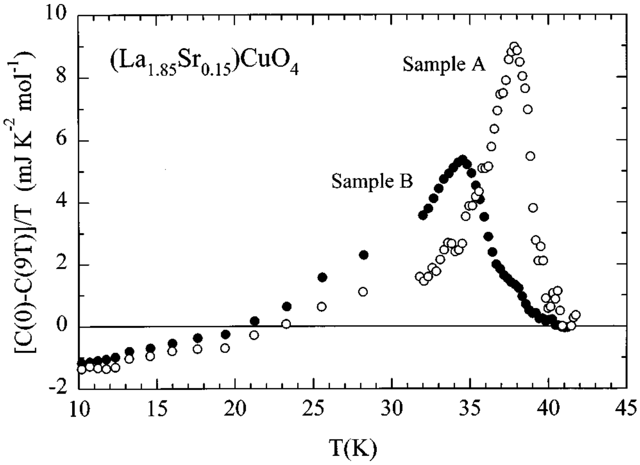

FIG. 1. Specific-heat anomalies at T_c.

though the specific heats differ significantly in other respects, the *d*-wave related effects observed in these samples are essentially identical, suggesting that they are intrinsic properties characteristic of the superconducting state. Reports of a preliminary analysis of the data for one sample have been presented at several conferences.[13] The somewhat different conclusions reported here are based on a more rigorous analysis of the data. (Data for 0.1 T, which contributed to an erroneous conclusion in the earlier reports,[13] have been omitted in this paper because of uncertainty in the 0.1-T heat capacity of the sample holder.)

The samples were polycrystalline and ~0.5 g in mass. Measurements were made in a calorimeter used recently for measurements on YBCO.[5,11] The thermometer calibration and tests of the accuracy of the results were similar to those described briefly in connection with earlier measurements.[3] The values of $\gamma^*(0)$ and the magnitudes of the anomalies at T_c vary widely for LSCO samples, suggesting the presence of variable, but often large, amounts of nonsuperconducting material[14] that would compromise any interpretation of C in terms of *d*-wave effects. The relatively small values of $\gamma^*(0)$ (see below) and the relatively sharp and large anomalies at T_c (in comparison with those for other LSCO samples), particularly for sample A (see Fig. 1) attest the quality of these samples and their appropriateness for a study of the *d*-wave effects.

For a cuprate superconductor, $C(H,T)$ includes four ‘‘background’’ contributions in addition to $C_{\rm DOS}$: $C_{\rm lat}(T)$, the lattice contribution; $\gamma^*(0)T$, the zero-field T-proportional term; $C_{\rm hyp}(H,T)$, the hyperfine contribution; $C_{\rm mag}(H,T)$, the PC contribution (see, e.g., Refs. 5 and 11 for a discussion). For comparison with the theoretical predictions it is convenient to organize the contributions to $C(H,T)$ in a form suggested by Eq. (2),

$$C(H,T)/T^2 = C_{\rm DOS}(H,T)/T^2 + \Delta(T) + \delta(H,T), \qquad (3)$$

where $\Delta(T) = [C_{\rm lat}(T) + \gamma^*(0)T]/T^2$ and $\delta(H,T) = [C_{\rm hyp}(H,T) + C_{\rm mag}(H,T)]/T^2$ represent, respectively, the H-independent and H-dependent background contributions. Raw data for representative fixed T's are plotted as $C(H,T)/T^2$ vs $H^{1/2}/T$ (the + symbols) in Fig. 2. For each T the eight points represent the data for the eight values of H. (The data were taken at very close to the same T's for all H, and small interpolations to the T's for $H=0$ were made for the $H\neq 0$ data.) If $C_{\rm DOS} = \beta H^{1/2}T$, as predicted for a range of H that does not include $H=0$, and if $C_{\rm hyp}$ and $C_{\rm mag}$ were negligible, those points would fall on parallel straight lines with the slope β, and $H=0$ intercepts at $[C_{\rm lat}(T) + \gamma^*(0)T]/T^2$ for that T. If there were in addition a nonzero contribution, αT^2, to $C_{\rm DOS}(H,T)$ at $H=0$, the $H=0$ point would fall above the $H=0$ intercept of the straight line by an amount α. In fact, the points representing the raw data do conform qualitatively to these expectations. The evident discrepancies, which are more significant at the lower temperatures, can be attributed to $C_{\rm mag}$ and $C_{\rm hyp}$.

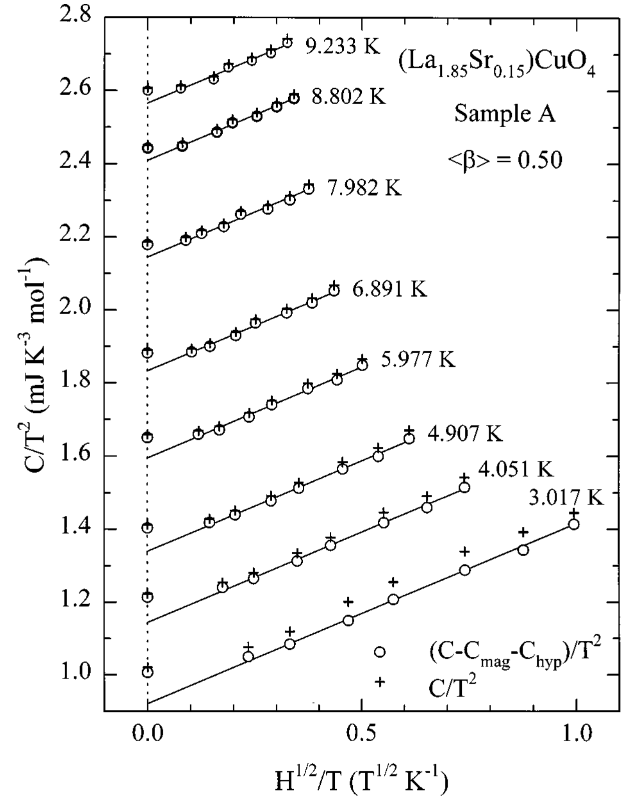

FIG. 2. The specific-heat of sample A for representative temperatures and eight magnetic fields, 0–9 T. The + symbols represent raw data; the open circles represent data corrected for paramagnetic-center and hyperfine contributions. See text for discussion.

Refinement of the analysis of the data require analytical expressions for $C_{\rm hyp}$ and $C_{\rm mag}$. $C_{\rm hyp}$, which is important only at the lowest T, has the form $D(H)T^{-2}$, but there is no obvious analytical expression for $C_{\rm mag}$. Just as for YBCO (Refs. 3 and 11) the low-T data could not be fitted with the simple Schottky expressions for $C_{\rm mag}$ that would be expected for spin-$\frac{1}{2}$ PC's. For YBCO the problem was resolved by the recognition that there were singlet-ground-state PC's,[15] as well as spin-$\frac{1}{2}$ PC's, and the use of ESR-derived parameters[16] to obtain an expression for their low-T contribution to $C_{\rm mag}$. Although $C(H,T)$ for LSCO also suggests the presence of singlet-ground-state PC's, the data are not well represented by the ESR parameters used for YBCO (and there is no reason to expect that they would be). Without independently determined spin-Hamiltonian parameters it was not possible to find an analytical expression for $C_{\rm mag}$ that accounted for

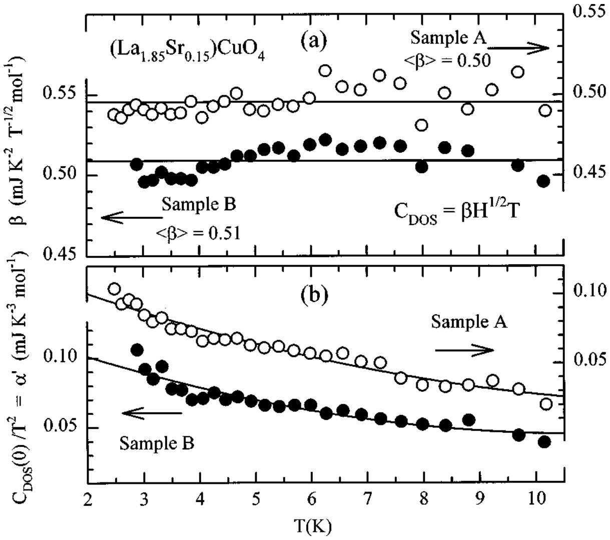

FIG. 3. (a) Values of β, the slopes of the straight lines in Fig. 1. (b) Values of $\alpha' \equiv C_{DOS}(0)/T^2$, where the curves are guides to the eye. See text for discussion.

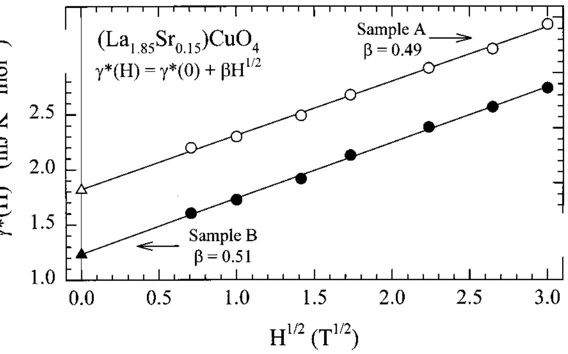

FIG. 4. The $H^{1/2}$ dependence of $C_{DOS}/T = [\gamma^*(H) - \gamma^*(0)]$ for $H \neq 0$. See text for discussion.

the data at the lowest T. However, the effect of the $H=0$ splitting of the PC levels becomes less important with increasing T. Accordingly, the analysis was restricted to $2.5 \leqslant T \leqslant 10\,\mathrm{K}$ for sample A and $3 \leqslant T \leqslant 10\,\mathrm{K}$ for sample B, where the data were adequately represented with spin-$\frac{1}{2}$ Schottky functions with $g=2.1$. The concentrations of PC's, 0.96×10^{-4} and 1.7×10^{-4} mol (mol LSCO)$^{-1}$ for samples A and B, respectively, and the parameters for C_{hyp} were obtained from global fits. Essentially the same concentrations of PC's were obtained in single-field fits for $H=3$, 5, and 7 T, the fields in which C_{mag} is most important. These contributions were subtracted from $C(H,T)$, and the points thus corrected plotted as the open circles in Fig. 2. All further analysis was based on these corrected points.

For each T and for $H \geqslant 1$ T the corrected data points were fitted with the straight line shown in Fig. 2. The derived values of β are essentially independent of T [see Fig. 3(a)], corresponding to $C_{DOS}(H) = \beta H^{1/2} T$ with $\langle\beta\rangle = 0.50$ and 0.51 mJ K^{-2} T$^{-1/2}$ mol^{-1} for samples A and B, respectively. Although the 0.5-T data were omitted from these fits, they fall very close to the lines, and their inclusion in the fits has a negligible effect on the derived values of β. C_{lat} and $\gamma^*(0)$ were obtained by fitting the $H=0$ intercepts of the lines, $\Delta(T) = [C_{lat} + \gamma^*(0)T]/T^2$, with $C_{lat} = B_3T^3 + B_5T^5 + B_7T^7$, to obtain $\gamma^*(0) = 0.44$ and 1.23 mJ K^{-2} mol^{-1} and $B_3 = 0.259$ and 0.221 mJ K^{-3} mol^{-1} for samples A and B, respectively. C_{DOS} was then obtained for all H and T as $C_{DOS} = C - C_{mag} - C_{hyp} - T^2\Delta(T)$. A somewhat different way of demonstrating the consistency of the $H \neq 0$ data with $C_{DOS}(H) = \beta H^{1/2} T$ is shown in Fig. 4. For each nonzero H, including 0.5 T, for which the data were omitted from the fits in Fig. 2, an average value of $\gamma^*(H)$ was obtained by averaging C_{DOS} over all T's. These values and $\gamma^*(0)$ are plotted vs $H^{1/2}$. Least-squares fits to $\gamma^*(H)$, including $\gamma^*(0)$, give essentially the same values of β as the averages of the values obtained in the constructions in Fig. 2. This figure emphasizes the accuracy with which the data for $0.5 \leqslant H \leqslant 9$ T conform to the predicted $H^{1/2}T$ dependence.

For $H=0$, C_{DOS} is represented in Fig. 3(b) as $\alpha'(T) \equiv C_{DOS}/T^2$. Although there is a well defined, nonzero value of $C_{DOS}(0)$, as is also apparent in Fig. 2, it is not proportional to T^2, as shown by the T dependence of α'. At the lowest T, it is possible that the apparent values of α' reflect small errors in the correction for C_{mag} and C_{hyp}, but that effect would decrease rapidly with increasing T. It is possible that impurities contribute to the deviations of $C_{DOS}(0)$ from a T^2 behavior,[9] but for YBCO it seems that at least some impurities produce normal regions without affecting the parameters characterizing the superconducting regions of the sample.[5] Another possibility is that the order parameter is not purely d wave, but mixed, modifying the shape of the "nodes." Perhaps most importantly, however, the predicted T^2 dependence is a low-T approximation that is probably not valid to 10 K, which is $\sim T_c/4$. For YBCO the T^2 dependence is reasonably well defined to $T_c/10$.[5] Given these considerations, and the assumption that the limiting low-T behavior of $C_{DOS}(0)$ is T^2, as it is in YBCO,[2,5] a reasonable estimate of the value of the coefficient is $\alpha \sim 0.09$ mJ K^{-3} mol^{-1}, the value of α' for both samples at 3 K, which is $\sim T_c/10$.

The data are compared with the scaling relation in Fig. 5. Figure 5(a) demonstrates the collapse onto a single straight line, $C_{DOS} = \beta H^{1/2} T$, of the individual data points for $H \neq 0$. The plot in Fig. 5(b) permits the inclusion of the $H=0$ data, which are represented by vertical bars that give the range of values of α'. In the corresponding plot for YBCO the points for low nonzero values of $H^{1/2}/T$ deviate from the straight line in a way that suggests a smooth crossover to the $H^{1/2}/T=0$ data.[5] Although there is no such evidence for the crossover in Fig. 5(b), it could well occur in the region in $H^{1/2}/T$ in which there are no data. The absence of data points in that region and the uncertainty in the value of α notwithstanding, both Figs. 5(a) and 5(b) are consistent with the predicted scaling.

The observation of a nonzero $C_{DOS}(0)$ reported here for $x=0.15$ is at variance with the conclusion of Chen *et al.*[17] who measured $C(H)$ for $x=0.16$ and found no evidence of such a term. The discrepancy may arise in part from differences in the precision of the data [compare Fig. 5(a) with their Fig. 4], but differences in the data analysis are probably at least as important. They based their conclusion on a single-$H(H=0)$ fit and represented C_{mag} (the concentration of PC's was similar to that of sample A) by a simple Schottky anomaly for $T \geqslant 0.6$ K. Even random scatter in the

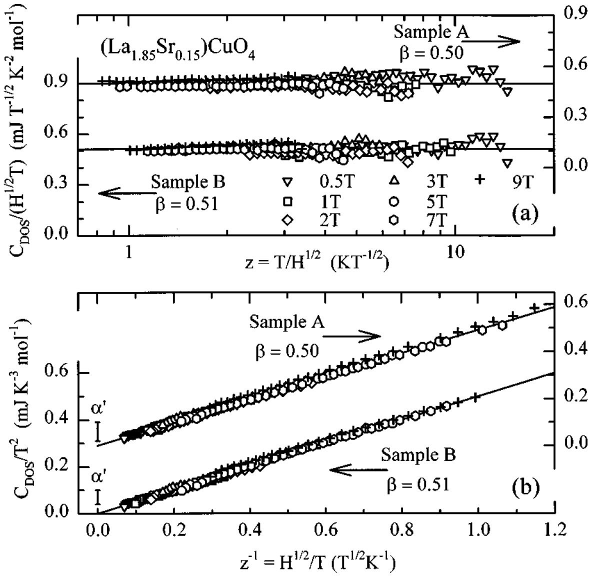

FIG. 5. Test of the scaling relation: (a) as represented by Eq. (1), for $H \neq 0$ data and (b) as represented by Eq. (2), with $H=0$ data included.

data is more likely to lead to an erroneous conclusion about the T^2 term in a single-H fit than a global fit.[18] Furthermore, the data reported here suggest that the Schottky anomaly would not be an adequate representation of C_{mag}, increasing substantially the probability of uncertainty or error. Chen *et al.* *were* able to resolve a *larger* T^2 term, $\alpha = 0.31\,\mathrm{mJ\,K^{-3}\,mol^{-1}}$, for $x=0.22$, which could be consistent with the estimate of $\alpha = 0.09\,\mathrm{mJ\,K^{-3}\,mol^{-1}}$ reported here for $x=0.15$ and the expectation[19] that α would be approximately the same for underdoped- and optimally doped samples, but larger for overdoped samples. Their conclusions about the H dependence of C_{DOS} for $H \neq 0$ were similar to those reported here [compare Figs. 4 and 5(a) with their Figs. 2(a) and 4]. The substantially higher values of α reported by Momono *et al.*[20] are of questionable reliability because they appear to be based on the assumption that C_{lat} is the same for superconducting and Zn-doped, nonsuperconducting samples. In fact, C_{lat} for both YBCO and LSCO is remarkably sensitive to doping, and even to details of sample preparation (C_{lat} differs by 17% for the two LSCO samples described in this paper).

In summary, the electron-density-of-states contribution to the specific heat of $(La_{1.85}Sr_{0.15})CuO_4$ shows, with a high degree of accuracy, the $H^{1/2}T$ dependence expected for line nodes in the energy gap and $H \neq 0$, and conformity to a scaling relation predicted for a *d*-wave order parameter for all H. The existence of a finite contribution for $H=0$, also expected for line nodes, is clearly established but its small size precludes a precise determination of its temperature dependence. The similarity of these features for two samples that differ in other respects gives confidence that they are intrinsic properties characteristic of the superconducting state.

The work at Lawrence Berkeley National Laboratory was supported by the Director, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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