Temperature Dependence of Upper Critical Field as an Indicator of boson Effects in Superconductivity in Nd$_{2−x}$Ce$_x$CuO$_{4−y}$

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The temperature dependence of upper critical field $B_c$ was determined from the shift of resistive transition $\Delta T(B)$ in nearly optimally doped Nd$_{2−x}$Ce$_x$CuO$_{4−y}$ single crystals. Within the experimental accuracy, the weak-field data are described by power function $B_c \propto (\Delta T)^{3/2}$. This result is compared with the data on heat capacity and analyzed in the context of possible manifestations of boson effects in superconductivity. The $T$ dependence of $B_c$ persists down to the lowest temperatures, but the numerical values of $B_c$ below 1 K are different for different samples.

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There are grounds to believe that high-temperature superconductivity (HTSC) is not described by the BCS theory. One of them consists in the relationship between the density of Cooper pairs and the coherence length $\xi$ (the pair size). In HTSC cuprates, superconductivity is due to the carriers in the CuO$_2$ plane. In all 2D systems, the density of states $g_F$ at the Fermi level in the CuO$_2$ plane does not depend on the carrier concentration in the normal state and, according to measurements, is equal to $g_F = 2.5 \times 10^{-4}$K$^{-1}$ per one structural unit of CuO$_2$ (this value is nearly the same for all cuprate families, see, e.g., [1], Ch. 13). Assuming that the superconducting gap $\Delta$ is of the order of transition temperature $T_c$, one estimates the mean distance $r = n^{-1/2} \approx (g_F \Delta)^{-1/2}$ between the pairs in the CuO$_2$ plane at 25 Å for $T_c \approx 100$ K and 75 Å for $T_c \approx 10$ K. These $r$ values should be compared with the typical coherence length $\xi \approx 20$ Å in the ab plane [1], so that $r \gg \xi$ in the HTSC materials. Inasmuch as the BCS theory introduces Cooper pairs to describe the Fermi-liquid ground state as a whole, its validity for the description of HTSC is not obvious. This causes interest in the models of Bose superconductivity for which $r \gg \xi$ and which are based on Bose-Einstein condensation (BEC) in a system of charged bosons [2-4]. The experimental evidences for the boson effects in HTSC are presently intensively accumulated.

One such evidence can be expected to obtain from the measurements of the temperature dependence of magnetic field $B_c$ destroying superconductivity. In the BCS theory, the $B_c(T/T_c)$/$B_c(0)$ function is linear in the vicinity of $T/T_c = 1$; it monotonically increases to saturation near the zero temperature and almost coincides with the limiting value even at $T/T_c = 0.2$ [5]. However, in most cases, the HTSC materials behave in a different manner and demonstrate positive second derivative $\partial^2 B_c/\partial T^2$ over the entire temperature range.

The $B_c(T)$ measurements are mainly based on an analysis of the resistive transition. Two types of behavior are known for the resistive transition of HTSC materials in a magnetic field. For one of them, the transition is sizably broadened in a magnetic field, so that it is hard and even practically impossible to gain from it any information about the $B_c(T)$ dependence. The other transition is shifted in a magnetic field to lower temperatures and either remains undistorted, as in usual superconductors, or undergoes an insignificant distortion. This usually occurs for those members of HTSC families in which $T_c < 20$ K. The transition shift in these materials is naturally explained by the field-induced destruction of superconductivity. Irrespective of the mechanism of dissipative processes in the superconducting state, the spectrum rearrangement and the appearance of superconducting pairing should necessarily affect the $R(T)$ resistance. With this preposition, one can readily construct the $B_2(T)$ function.

Almost in all HTSC cuprates such as the Tl-based [6] and Bi-based [7] families and the LaSrCuO [8] and Nd(Sm)CeCuO [9-11] families, as well as in the Zn-doped [12] or oxygen-deficient [13] YBaCuO, the $B_c(T)$ function derived from the shift of resistive transition has the positive second derivative over the whole temperature range $0 < T/T_c < 1$ and shows a tendency to diverge at small $T/T_c$ values. Most discussion over the $B_c(T)$ curves concentrated precisely on this divergence and considered it as the most dramatic departure from the BCS theory. At the same time, the behavior of the $B_c(T)$ function near $T_c$ is also quite informative. Contrary to expectations, almost in all cases where the field-induced resistive-transition shift in HTSC cuprates preceeds in a parallel manner, the experimental data indicate that the $\partial B_c/\partial T$ derivative is zero at the $T_c$ point [6-13]. The $\partial B_c/\partial T$ derivative of critical field in the $T_c$ point is related to the free energy $F$ and heat capacity $C$ in this point by the well-known Rutgers formula:

$$\frac{1}{4\pi} \left(\frac{\partial B_c}{\partial T}\right)_{T_c}^2 = \frac{\partial^2}{\partial T^2} (F_s - F_n) = \frac{C_s - C_n}{T_c}. \quad (1)$$

Inasmuch as the thermodynamic critical field $B_c$ is different from the upper critical field $B_{c2}$, Eq. (1) can be used only for qualitative estimates. However, being based on thermodynamics, this equation is very useful.

In usual superconductors, $F_s - F_n \propto (T_c - T)^2$, so that the heat capacity undergoes a jump and $B_c$ is linear in $(T_c - T)$. In the BEC case, $F_s - F_n \propto (T_c - T)^3$, so that the heat capacity is a continuous function in the
transition point [14]. It then immediately follows that 
\[ \partial B_c / \partial T = 0 \] and
\[ B_c \propto (T_c - T)^{3/2}. \] (2)

Of course, one can hardly imagine that the Fermi gas 
suddenly and completely transforms into a Bose gas at 
low temperatures. It was assumed in [4] that bosons 
appear in small pockets of the k-space near the Fermi 
level. In the isotropic model, one can only speak about 
pairing of sufficiently energetic fermions, as in the BCS 
theory. This kind of model has been proposed in [15]. 
Nevertheless, Eq. (2) deserves a serious experimental 
verification.

Such was the motivation of our work consisting in the 
measurement and analysis of the field-induced shift of 
resistive transition in Nd\(_{2-x}\)Ce\(_x\)CuO\(_{3-x}\) single crystals. 
We will discuss separately the behavior of the B\(_{c2}\) field 
in the vicinity of T\(_c\) and at low temperatures.

**Experiment.** (NdCe)\(_2\) CuO\(_4\) single crystals were 
grown from a mixture of components taken in the mo-
lar ratio Nd\(_3\)O\(_3\); CeO\(_2\); CuO = 1:0.05:11 in a crucible 
made from yttrium-stabilized zirconium dioxide. The 
use of a modified growth regime markedly reduced the 
time of interaction between the melt and the crucible at 
high temperature. Owing to the accelerated-decelerated 
crystallization front (dT/dx ≥ 10 K/cm), after which the 
crucible was decanted and cooled at a rate of 30-50 
K/h to ambient temperature. The crystals were shaped 
like platelets of thickness 20-40 mm. Their composition 
Nd\(_{1.82}\)Ce\(_{0.18}\)CuO\(_2\) was determined by local X-ray spec-
troscopic analysis. The analysis revealed Zn traces in the 
crystals at a level of 0.1 wt %. Initially the crystals did 
not show superconducting transition above 4.2 K. The 
superconducting transition at T\(_c\) ≈ 20 K appeared after 
15-h annealing at 900 °C in an argon atmosphere.

Measurements were made for two plates approximately 
1 × 2 mm in size. The silver paste contacts were fused 
in the air at a temperature of 350 °C. Four contacts in 
sample 1 were arranged 0.5 mm apart in a row on one 
side of the plate. The potential contacts in sample 2 
were placed on the opposite side of the plate beneath 
the current contacts, allowing the measuring current to be 
directed both along and transversely the ab plane. This 
did not affect the results. The resistance was measured 
by the standard method using a lock-in nanovoltmeter at 
a frequency of 13 Hz. The measuring current was small 
for the linear regime and the absence of overheating 
to be provided down to the lowest temperatures. The 
magnetic field was directed along the normal to the plate 
(c axis). Measurements were performed over the temper-
ature range from 25 K to 25 mK. The onset of zero-field 
superconducting transition in both samples occurred at 
about 20.5 K.

The measurements gave identical results for both sam-
ple. Figure 1 demonstrates a series of low-field R(T) 
curves for sample 2. At high temperatures, all curves 
show the same asymptotic behavior R\(_n\)(T) above the 
transition, and one can assume that the R\(_n\) function 
does not depend on B at T > 10-12 K. The zero-field 
transition shows a certain structure, which, however, is 
smoothed out even at 100-200 Oe. The field effect mainly 
amounts to shifting the transition to lower temperatures.
The degree in which this shift is parallel can be checked 
by comparing the shift of the onset of transition with 
the shifts of the

\[ \Delta T = T_{c1} - T \]

by different symbols in Fig. 2a for all four lev-
els. The systematic deviations of the symbols from the

\[ R_n(T) \]

\[ B = 7 kOe, 6, 5, 4, 3, 2, 1.5, 0.8, 0.4, 0.2, 0.1, 0 \]

\[ T_{c0.5} \]

\[ 0.67 \]

\[ 0.5 \]

\[ Level 0.2 \]

\[ 2.0 \]

\[ 1.5 \]

\[ 1.0 \]

\[ 0.5 \]

\[ 0.2 \]

\[ 0.1 \]

\[ 0 \]

\[ 0.67 \]

\[ 0.5 \]

\[ Level 0.2 \]

\[ 2.0 \]

\[ 1.5 \]

\[ 1.0 \]

\[ 0.5 \]

\[ 0.2 \]

\[ 0.1 \]

\[ 0 \]

\[ sample 2 \]

\[ FIG. 1. The R(T) curves for sample 2 in magnetic fields \]

\[ (from right to left) from 0 to 7 kOe. The dashed lines are the \]

\[ straight line R_n(T) and the straight lines at the levels of 0.67, \]

\[ 0.5, and 0.2 of R_n(T). The method of determining the onset \]

\[ of transition is demonstrated and the T_{ci} fields from which \]

\[ the shifts are measured are shown \]

\[ 1 \]The low-temperature measurements in strong magnetic 
fields were carried out at the NHMFL (Tallahassee, Fla., 
USA).
straight line
\[ B_{c2} = (\Delta T)^\beta, \]  
constructed by averaging the results for all points are small for each of the symbols. This implies that the distortions of the transition shape are small as compared to its shift. The scatter of points in low fields is mainly caused by the fine structure of the \(R(T, B = 0)\) curve, which serves as a reference in the determination of the shift \(\Delta T\).

The coefficient \(\beta\) was determined from the slope of the straight line passing through the averaged \(\Delta T\) shifts (Fig. 2b). The curve processing for sample 2 (Fig. 1) yields \(\beta \approx 1.4\), and the processing of analogous curves for sample 1 yields \(\beta \approx 1.5\).

The resistances for both crystals decreased in a relatively narrow temperature range not to zero; one can see in Fig. 1 that, starting at the level of \(\sim 0.1\), a slanting tail appears. The same tail for sample 1 starts at a higher level of \(\sim 0.2\). In this work, we will analyze only the upper portion of the transition, assuming that the electron spectrum is rearranged into the form characteristic of the superconducting state precisely in this region.

Figure 3 shows the \(R(B)\) functions for very low temperatures \(T/T_c < 0.05\). In this region, the normal resistance depends, though weakly, on a magnetic field, while the onset of transition is clearly defined and its shift is easily detected even upon changing temperature below \(T/T_c = 0.005\). When considering the \(B_{c2}(T)\) functions in this region (see inset in Fig. 3), two fact are noteworthy. First, \(B_{c2}\) does not show tendency to diverge near zero temperature; although the derivative of \(B_{c2}(T)\) is large below 0.5 K, the function is linear within the experimental accuracy and extrapolated to a finite value \(B_{c2}(0)\) (similar result was obtained previously for thallium crystals [6]). Second, the critical fields at low temperature are equal to 69 and 80 kOe for samples 1 and 2, respectively, i.e., differ by more than 10%, inspite of the fact that the crystals were from the same batch and their \(T_c\) values coincide.

The graph of \(B_{c2}(T)\) over the entire temperature range is shown in the inset in Fig. 4; as in other HTSC cuprates, the second derivative \(\partial^2 B_{c2}/\partial T^2 \geq 0\) for all temperatures (cf., e.g., [6, 7]).

**Discussion.** It follows from the preceding section that our data for the vicinity of \(T_c\) are consistent, within the experimental accuracy, with Eq. (2). It would have been instructive to compare these data with the data on heat capacity, but, unfortunately, in the works where the heat capacity of \(\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4-y\) was measured [16] the contribution of critical fluctuations near \(T_c\) was not determined. Nevertheless, it is known that the measurements of heat capacity of the HTSC materials show strong dissimilarity from usual superconductors [17] but do not allow the discrimination between the BCS and BEC models. These problems can be illustrated by comparing the results of measurements of the resistance and heat capacity of the thallium high-\(T_c\) superconductor. No explicit jump in heat capacity is observed for this compound even at zero field, although the contribution from the critical fluctuations is undoubtedly present in the tempera-
ideal charged Bose gas, this contribution is hidden from view at the lower temperature where the transition occurs in magnetic field. Then, strange as it may seem, the resistive measurements provide the more reliable information on the transition position than the heat capacity measurements do.

According to the results obtained for the immediate vicinity of $T_c$, the behavior of the $B_{c2}(T)$ function should be compared with the predictions of the superconductivity models in a nonideal Bose gas. Due to the boson scattering by impurities or to the boson-boson interaction, the critical field in a weakly nonideal Bose gas behaves as [21]

$$B_{c2} \propto t^{-\alpha}(1 - t^{3/2})^{3/2}, \quad t = T/T_c, \quad (4)$$

where, depending on the particular model, the exponent $\alpha$ is equal to 1 or 3/2 [21, 22]. At $t \to 1$, function (4) takes the asymptotic form (2). It is seen in Fig. 4 that the experimental points deviate in the proper direction from the asymptote and, on the whole, correspond well to Eq. (4). A more detailed comparison is hardly pertinent, as long as the theories [21, 22] do not allow for the field-induced pair decay into fermions.

**Conclusions.** The field-induced distortion of the shape of resistive superconducting transition in the Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ single crystals is appreciably smaller than the transition shift. This allows the measurement of the $B_{c2}(T)$ function. As zero-field $T_c$ is approached, the $B_{c2}$ field behaves as a power function $B_{c2} \propto (\Delta T)^\beta$ with $\beta \approx 1.5$ and, correspondingly, with a horizontal tangent $\partial B_{c2}/\partial T = 0$. This should imply the absence of jump in heat capacity at the zero-field phase transition. Such a behavior is precisely that which is expected for the heat capacity and critical field in the BEC of a charged Bose gas. For this reason, one of the possible conclusions that can be drawn from such a behavior of $B_{c2}(T)$ near $T_c$ is that the description of superconductivity of the HTSC materials should involve the BEC elements, i.e., make allowance for the fact that fermions near the Fermi level tend to form bosons at temperatures above $T_c$. The $T$ dependence of $B_{c2}$ persists down to the lowest temperatures, although, probably, the $B_{c2}$ values in this region depend on lattice defects.

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