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Temperature Dependence of the Upper Critical Field as an Indicator of Boson Effects in Superconductivity in $Nd_{2-x}Ce_xCuO_{4-y}$

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The temperature dependence of the upper critical field B_{c2} was determined from the shift of the resistive transition $\Delta T(B)$ in nearly optimally doped $Nd_{2-x}Ce_xCuO_{4-y}$ single crystals. Within the experimental accuracy, the weak-field data are described by the power function $B_{c2} \propto (\Delta T)^{3/2}$. 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_{c2} persists down to the lowest temperatures, but the numerical values of B_{c2} below 1 K are different for different samples. © *2000 MAIK "Nauka/Interperiodica".*

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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 n of Cooper pairs and the coherence length ξ (the pair size). In HTSC cuprates, superconductivity is due to the carriers in the CuO_2 plane. As 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 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 Δ is on the order of the 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 $r \gtrsim \xi$ in 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 superconductivity considering the boson limit $r \gg \xi$ and 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 being intensively accumulated.

One such piece of evidence can be expected from the measurements of the temperature dependence of the magnetic field B_{c2}, which destroys superconductivity. In the BCS theory, the $B_{c2}(T/T_c)/B_{c2}(0)$ 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, HTSC materials behave in a different manner and have a positive second derivative $\partial^2 B_{c2}/\partial T^2$ over the entire temperature range.

The $B_{c2}(T)$ 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, or even practically impossible, to gain any information about the $B_{c2}(T)$ dependence from it. 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 for which $T_c \lesssim 20$ 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 proposition, one can readily construct the $B_{c2}(T)$ function.

In almost 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 $B_{c2}(T)$ function derived from the shift of the resistive transition has a 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 discussions of the $B_{c2}(T)$ curves concentrated precisely on this divergence and considered it as the most dramatic

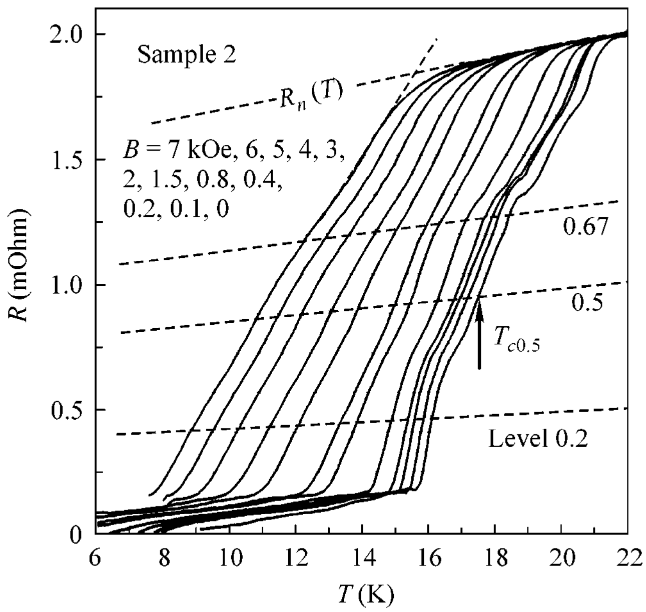

Fig. 1. The $R(T)$ curves for sample 2 in magnetic fields (from right to left) from 0 to 7 kOe. The dashed lines are the straight line $R_n(T)$ and the straight lines at the levels of 0.67, 0.5, and 0.2 of $R_n(T)$. The method of determining the onset of the transition is demonstrated, and the T_{ci} fields from which the shifts were measured are shown.

departure from the BCS theory. At the same time, the behavior of the $B_{c2}(T)$ function near T_c is also quite informative. Contrary to expectations, in almost all cases where the field-induced resistive-transition shift in HTSC cuprates proceeds in a parallel manner, the experimental data indicate that the $\partial B_{c2}/\partial T$ derivative is zero at the T_c point [6–13].

The $\partial B_c/\partial T$ derivative of the critical field at the T_c point is related to the free energy F and heat capacity C at this point by the well-known Rutgers formula:

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

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, $F_s - F_n \propto (T_c - T)^3$ and the heat capacity is a continuous function at the transition point [14]. It then immediately follows that $\partial B_c/\partial T = 0$ and

$$B_c \propto (T_c - T)^{3/2}. \qquad (2)$$

Of course, one can hardly imagine that a 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. Nevertheless, Eq. (2) deserves serious experimental verification. Such was the motivation of our work consisting in the measurement and analysis of the field-induced shift of the resistive transition in $Nd_{2-x}Ce_xCuO_{4-y}$ single crystals. We will discuss separately the behavior of the B_{c2} field in the vicinity of T_c and at low temperatures.

Experiment. $(NdCe)_2CuO_4$ single crystals were grown from a mixture of components taken in the molar ratio $Nd_2O_3 : CeO_2 : CuO = 1 : 0.05 : 11$ 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 temperatures. Owing to the accelerated–decelerated crucible rotation, the melt was intensively stirred so that the homogenization time for the molten solution did not exceed 1 h at a temperature near 1150°C. The growth was carried out for several hours upon slow cooling (6 K/h) under the conditions of a morphologically stable crystallization front ($dT/dx \geq 10$ K/cm), after which the crucible was decanted and cooled at a rate of 30–50 K/h to the ambient temperature. The crystals were shaped like platelets 20–40 μm thick. Their composition—$Nd_{1.82}Ce_{0.18}CuO_x$—was determined by local X-ray spectroscopic analysis. The analysis revealed Zn traces in the crystals at a level of 0.1 wt %. Initially, the crystals did not show a superconducting transition above 4.2 K. The superconducting transition at $T_c \approx 20$ K appeared after 15 h of 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 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 transverse to 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 enough to provide the linear regime and the absence of overheating down to the lowest temperatures. The magnetic field was directed along the normal to the plate (c axis). Measurements were performed over the temperature range from 25 K to 25 mK.[1] The onset of the zero-field superconducting transition in both samples occurred at about 20.5 K.

The measurements gave identical results for both samples. 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

[1] The low-temperature measurements in strong magnetic fields were carried out at the NHMFL (Tallahassee, Fla., USA).

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 to which this shift is parallel can be checked by comparing the shift of the onset of the transition with the shifts of the $R(T)$ function at different levels: $0.2R_n$, $0.5R_n$, and $0.67R_n$ (see curves in Fig. 1). For the parallel shift, all constructions in Fig. 1 should give the same function $B_{c2}(\Delta T)$, where $\Delta T = T_{ci} - T$ and T_{ci} is the temperature corresponding to the same level on the initial curve $R(T, B = 0)$. The log–log plots of the shifts are shown by different symbols in Fig. 2a for all four levels. The systematic deviations of the symbols from the straight line

$$B_{c2} = (\Delta T)^{\beta} \quad (3)$$

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 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 ΔT. The coefficient β was determined from the slope of the straight line passing through the averaged ΔT shifts (Fig. 2b). 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 to a nonzero value; one can see in Fig. 1 that, starting at the level of ~0.1, a slanting tail appears. The same tail for sample 1 starts at a higher level of ~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 typical 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 the magnetic field, while the onset of transition is clearly defined and its shift is easily detected even upon changing the temperature below $T/T_c = 0.005$. When considering the $B_{c2}(T)$ functions in this region (see inset in Fig. 3), two facts are noteworthy. First, B_{c2} does not show a 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 is extrapolated to a finite value $B_{c2}(0)$ (a 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., they differ by more than 10%, in spite of the fact that the crystals were from the same batch and their T_c values coincided.

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]).

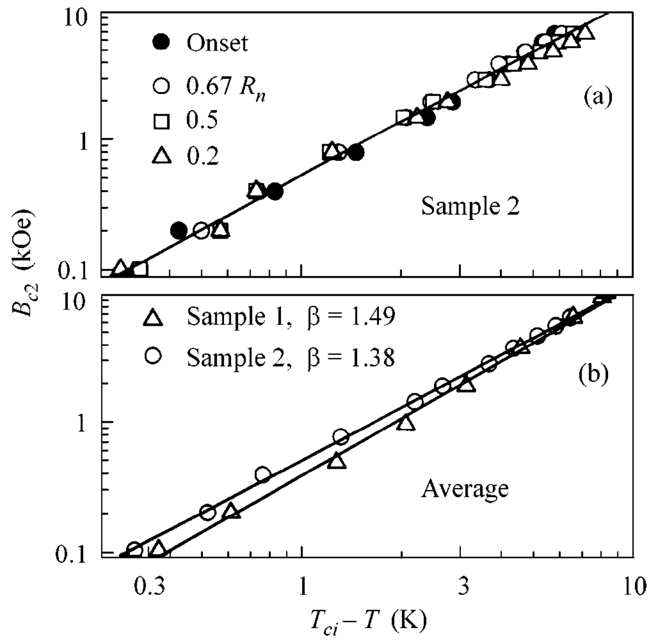

Fig. 2. (a) Plots of the field vs. shift at different levels in this field; (b) the same for the averaged shifts for two samples.

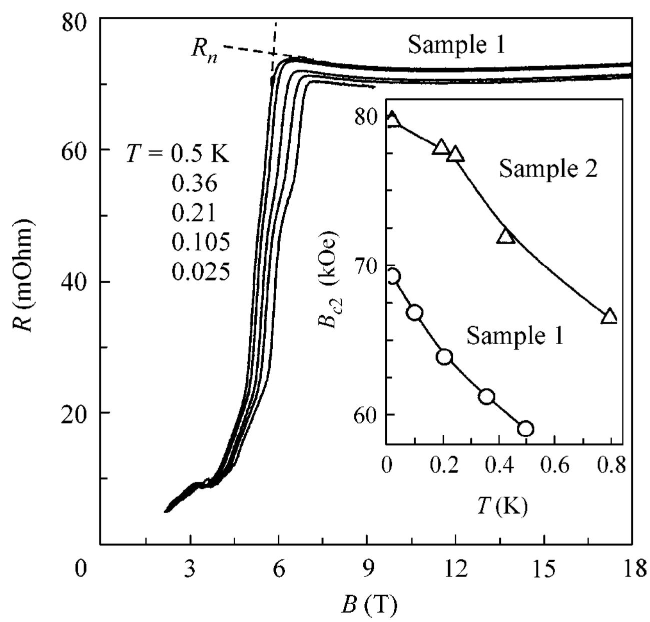

Fig. 3. The $R(B)$ curves for sample 1 at temperatures (from left to right) from 0.5 K to 25 mK. Inset: the field of the onset of transition at low temperatures for both samples.

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 $Nd_{2-x}Ce_xCuO_{4-y}$ was measured [15], the contribution of critical fluctuations near T_c was not

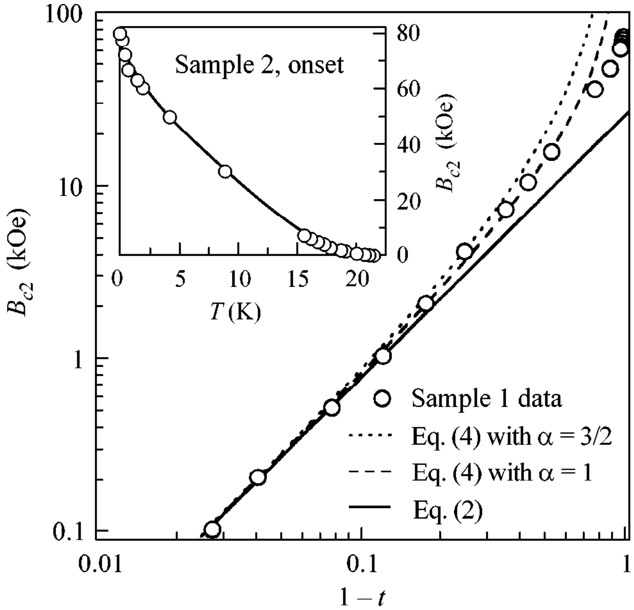

Fig. 4. Comparison of the experimental B_{c2} values for sample 1 with Eqs. (2) and (4). Inset: the $B_{c2}(T)$ function for sample 2 over the entire temperature range. The line is a guide to the eye.

determined. Nevertheless, it is known that the measurements of heat capacity of HTSC materials show strong dissimilarities to usual superconductors [16] 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 temperature range 16–10 K [17]; this contribution is reduced by approximately one-half in a field of 0.4 T and remains virtually unchanged with changing temperature. At the same time, the resistive measurements made by the same experimental group [6] suggest that a field of 0.4 T shifts the transition by 25% from 16 to 12 K.

In connection with this contradiction, an interesting remark was made in [18], where numerical calculations were carried out for the heat capacity of an ideal charged Bose gas in a weak magnetic field. It is well-known that BEC does not occur in an ideal charged Bose gas in a uniform magnetic field [19], because the density of states diverges at the lower Landau level of the spectra of charged bosons. This implies that the transition occurs only at an isolated point in the (T, B) plane. The magnetic field in this plane is scaled by the comparison of the cyclotron energy $\hbar eB/mc$ with T_c. Substituting the free electron charge and mass for e and m, respectively, one arrives at the value of 8 T for the characteristic field at T_c = 16 K. On this scale, the above-mentioned field of 0.4 T is as small as 0.05. As long as the field is low, the phase trajectory again passes through the vicinity of the transition point in the (T, B) plane upon changing T, but, as the field increases, the "impact parameter" increases, while the contribution of critical fluctuations decreases. However, the temperature interval corresponding to the small impact parameters does not change. In the case that the transition is BEC in a weakly nonideal charged Bose gas, this contribution is hidden from view at the lower temperature where the transition occurs in a magnetic field. Then, strange as it may seem, resistive measurements provide more reliable information on the transition position than 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 boson scattering by impurities or to the boson–boson interaction, the critical field in a weakly nonideal Bose gas behaves as [20]

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

where, depending on the particular model, the exponent α is equal to 1 or 3/2 [20, 21]. At $t \longrightarrow 1$, 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 [20, 21] do not allow for field-induced pair decay into fermions.

Conclusions. The field-induced distortion of the shape of the resistive superconducting transition in the $Nd_{2-x}Ce_xCuO_{4-y}$ single crystals is appreciably smaller than the transition shift. This allows the measurement of the $B_{c2}(T)$ function. As T_{c0} 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 a jump in heat capacity at the zero-field phase transition. Such behavior is precisely that which is expected for the heat capacity and critical field in BEC of a charged Bose gas. For this reason, one of the possible conclusions that can be drawn from such behavior of $B_{c2}(T)$ near T_c is that the description of superconductivity of HTSC materials should involve the BEC elements, i.e., should 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 the B_{c2} values in this region probably depend on lattice defects.

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