Anomalous Magnetic Field Dependence of the Thermodynamic Transition Line in the Isotropic Superconductor (K,Ba)BiO$_3$

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The $H - T$ phase diagram of high $T_c$ superconducting oxides has been the focus of intense theoretical and experimental study during the past decade [1]. One of the most interesting phenomenon which has been observed is the existence of a melting line $T_m(H)$ above which the vortex lattice melts into a liquid of entangled lines [2]. This melting has very important consequences for the physics of vortices, since the free motion of the flux lines in the liquid state gives rise to a large dissipation and renders the system useless for applications. The presence of this liquid phase also hinders any direct determination of the upper critical field $H_{c2}$ from standard magnetotransport data. Indeed, any resistive “critical” field $H_R(T)$ defined as the field for which the resistivity reaches some arbitrary value $R$ (e.g. 50% of the normal state resistivity), then presents a positive curvature in high $T_c$ cuprates [3] as well as in (K,Ba)BiO$_3$ [4, 5].

Similarly, the presence of strong thermal fluctuations also complicates the determination of $H_{c2}$ from thermodynamic measurements. These fluctuations lead to broad and smooth anomalies in specific heat measurements ($C_p$). Thus the field $H_{Cp}$ (defined for instance by the inflexion point of $C_p/T$) can present either a positive curvature in $Y_{1}Ba_{2}Cu_{3}O_{7-δ}$ (YBCO) crystals [3], a linear dependence in $Tl_{2}Ba_{2}CuO_{6}$ [6] or even almost no dependence with field in highly anisotropic systems such as $Bi_{2}Sr_{2}Ca_{2}Cu_{3}O_{8}$ [7] and $HgBa_{2}Ca_{2}Cu_{3}O_{8+δ}$ [8]. It is still unclear whether this upper critical field still exists as a transition line or is just some smooth crossover between the vortex liquid and the normal state. In order to shed light on this issue, we performed thermodynamic (specific heat, magneto-tunneling, reversible magnetization) and transport measurements on high quality optimally doped $(K_x,Ba_{1-x})BiO_3$ single crystals ($x \sim 0.4$).

Thermal fluctuations are small in this system (the...
Ginzburg number $G_c$ is only $\sim 10^{-4}$ due to its isotropic structure, a $T_c \sim 31$K, and a coherence length on the order of 30 Å. Nevertheless, some of us have previously shown that the magneto-transport data is well described by the vortex-glass scaling formalism [4] suggesting that the vortex solid melts into a liquid at high temperature through a second order phase transition. In the following, the vortex-glass transition field $H_{vg}$ is defined as the field for which $R \to 0$. On the other hand, magnetotunneling measurements have shown that the superconducting gap $\Delta$ closes above some characteristic field $H_{\Delta}$. The corresponding $H_{\Delta}(T)$ line is in reasonable agreement with the classical Werthamer-Helfang-Hohenberg (WHH) theory for the upper critical field [3]. The physical image emerging from these measurements was then that of a liquid phase existing for $H_{vg} < H < H_{\Delta} \sim H_{c2}$. However, we will show here that the magnetic field $H_{Cp}$ is smaller than $H_{\Delta}$ and presents a strong positive curvature, indicating a very peculiar nature for the thermodynamic superconducting transition.

The measurements were performed on new particularly homogeneous single crystals presenting very sharp superconducting transitions in both transport ($\Delta T_c \sim 0.15$K) and ac susceptibility ($\Delta T_c \sim 0.2$K for $h_{ac} < 0.01$G) measurements. The specific heat was measured by an ac technique [4] which allows us to measure small samples (here a few $10^{-2}$ mm$^3$) with high sensitivity (typically 1 part in $10^4$). Heat was supplied to the sample at a frequency $\omega$ on the order of a few Hz by a light emitting diode via an optical fiber. The induced temperature oscillations were measured by a chromel-constantan thermocouple, which was calibrated in situ using a very pure silver single crystal as a reference. These measurements are only relative and were renormalized using the data from ref [5]. Figure 1 displays the temperature dependence of the specific heat at various magnetic fields up to 5T. The 7T curve is equal to the normal state specific heat above $T = T_c (H = 7T) \sim 20$K and has been used as a base line in Fig.1.

The unusually high quality of our crystals is attested to by the narrow width of the transition, which is on the order of 1K in zero magnetic field, and by the amplitude of the specific heat jump, $\Delta C_p(T_c)/T_c \sim 4 - 5$ mJ.mol$^{-1}$K$^{-2}$. This ratio is $\sim 2$ and 5 times larger than that of refs. [10] and [11], respectively, which are the only prior reports of a specific heat anomaly at $T_c$ in this system. This allowed us to study the magnetic field dependence of the specific heat anomaly in much greater detail. As shown in Fig.1, this anomaly remains well defined in magnetic fields. The $T_{C_p}(H)$ curve corresponding to any characteristic point of the transition (e.g. the onset, mid-point or maximum) presents a clear positive curvature. This can be seen in Fig.2 where $T_{C_p}$ corresponds to the onset of the peak. The shaded area represents the temperature difference between the onset and the mid-point of the transition. A very similar upward curvature has been obtained in two other samples. A positive curvature was already obtained by transport [4] and magnetic measurements [12]. However, in non-classical superconductors, there is an ambiguity in defining $H_{c2}$ using those techniques.

Another striking feature of the specific heat anomaly is the rapid collapse of its height with field. Such a behaviour was previously observed in high $T_c$ materials [8] and is usually attributed to the presence of highly field dependent thermal fluctuations. The observation of a similar collapse in $(K, Ba)BiO_3$ remains a puzzling issue. Geometrical arguments based on entropy conservation imply that this reduction must be accompanied by a rapid, anomalous, increase of the specific heat at low temperature for fields much smaller than the upper critical field of $\sim 30$T deduced from transport data. The data from ref [10] also suggest such a behaviour.

As pointed out above, the specific heat measurements are in striking contrast with our previous magneto-tunneling [3] data which suggested that the upper critical field (defined as the field $H_{\Delta}$ for which the superconducting gap is completely closed) presents a classical WHH dependence. We have thus performed similar magneto-tunneling measurements on the sample which has been used in the specific heat experiments. The inset of Fig.1 shows the evolution of the tunneling spectra near the normal state at $T = 20$K with increasing magnetic fields. $H_{\Delta}$ has been defined as the field for which the superconducting gap is completely closed ($H_{\Delta}(20$K$) \sim 10$T). As shown by the bold curve, at $H = H_{Cp}(20$K$) \sim 7$T, a gap some feature remains clearly visible in the cor-

![FIG. 2. $H - T$ phase diagram of the (K,Ba)BiO$_3$ system. Squares ($H_{Cp}(T)$): onset on the specific heat anomaly (see Fig.1, the shaded area represents the temperature difference between the onset and the mid-point of the anomaly), circles ($H_{vg}(T)$): "vortex-glass transition" line deduced from transport measurements ($R \to 0$), triangles: $H_{\Delta}(T)$ defined as the line for which the superconducting gap measures by tunneling spectroscopy vanishes. The different characteristic temperatures at 3T (arrows) as shown in Fig.3.](image-url)
responsing tunneling spectrum (bold curve). As shown in Fig.2, in agreement with our previous data, the curvature is much less pronounced for $H_\Delta$ and surprisingly $H_{vg} < H_{Cp}$, $H_\Delta$. Note that even though the difference between $T_{Cp}$ and $T_\Delta$ is quite large, the resistivity reaches about 95% of its normal state value ($R_N$) at $T_{Cp}$ and smoothly increases up to $\sim 100\%$ for $T \sim T_\Delta$ (see Fig.3). The specific heat anomaly thus defines a fundamental boundary below which the resistivity drops rapidly towards zero but superconductivity is only completely destroyed at $T = T_\Delta$ for which $R = R_N$ and the superconducting gap is completely suppressed. Note that the difference between $T_\Delta$ and $T_{Cp}$ is not due to sample homogeneities since heavy ion irradiation leads to an increase of $T_{Cp}$ which then tends towards $T_\Delta$. This difference could be due to the existence of a pseudo-gap but, in contrast to cuprates, this pseudo-gap would only occur in non zero magnetic field.

FIG. 3. Resistive transition at $H = 3T$. The onset of the specific heat anomaly (see Fig.1) corresponds to the temperature below which the resistivity rapidly decreases. $R \rightarrow R_N$ for $T = T_\Delta$ (temperature for which the superconducting gap closes, $R_N$ is the normal state resistivity). In the insert: renormalized specific heat vs temperature. As shown $T_{vg}$ is close to the mid-point of the specific heat anomaly.

To complete this study of the thermodynamic properties, we have performed reversible magnetization measurements ($M_{rev}$) using a SQUID magnetometer. In the intermediate magnetic field range, $H_{c1} \ll H \ll H_{c2}$, the reversible magnetization of extreme type-II superconductors in the London model is given by: $M_{rev} = -\frac{\alpha \Phi_0}{4\pi \lambda^2} \ln \left(\frac{\beta H_{c2}(T)}{H}\right)$ where $\alpha \sim 1$, $\Phi_0$ is the flux quantum, $\lambda(T)$ the magnetic penetration depth, $H_{c2}(T)$ the upper critical field and $\beta \sim 0.37$. Thus, $\partial M_{rev}/\partial \ln(H)$ is expected to be proportional to $1/\lambda^2(T) \sim (1-T/T_c)$ close to $T_c$. $M_{rev}$ presents a clear logarithmic dependence (see Fig.4) and the corresponding $\partial M_{rev}/\partial \ln(H)$ are shown in Fig.4. However, as shown, strong deviations from the expected linear behaviour are visible and $\partial M_{rev}/\partial \ln(H)$ can be described much better by a $(1-T/T_c)^{1.5}$ law (solid line, the dotted line is a WHH dependence for $1/\lambda^2$). A similar deviation is usually observed in high $T_c$ cuprates and has been attributed to the presence of strong fluctuations. It was originally suggested by Nelson et al. [18] that elastic distortions of the vortex lattice (in the presence of strong thermal fluctuations) may lead to a significant contribution to the entropy of the system. However the corresponding contribution to $\partial M_{rev}/\partial \ln(H)$ is expected to be of the order of $k_B T/\Phi_0 \xi$ [19] (where $k_B$ is the Boltzmann constant), which is about one order of magnitude smaller than the observed deviation in $(K, Ba)BiO_3$.

Both specific heat and reversible magnetization data thus point out the peculiar nature of the superconducting transition in $(K, Ba)BiO_3$. Moreover, as shown in Fig.2, $H_{vg}$ and $H_{Cp}$ present a very similar temperature dependence emphasizing the close relation between those two lines. As shown in the inset of Fig.3, the $R = 0$ criterion is close to the mid-point of the $C_p$ transition. This then suggests two possibilities: either (i) the positive curvature in $H_R$ is not due to the melting of the vortex solid as usually suggested but is an intrinsic property of the $H_{c2}$ line ($= H_{Cp}$) or (ii) the specific heat anomaly is not related to $H_{c2}$ but instead marks a transition in the vortex state. Many theoretical models have been developed in order to explain a "possible" upward curvature of the upper critical field in cuprates (including a spin-charge separation or very strong coupling) but none of those models can be applied to the $(K, Ba)BiO_3$ system. A positive curvature has also been predicted by Ovchinnikov and Kresin [20] in the presence of inhomogeneities and/or magnetic impurities. However, in this case this curvature is only expected to appear at low temperature (i.e. when the superconducting coherence length becomes smaller or on the order of the size of the impurity) and $H_{c2}$ is still expected to vary linearly with $T$ close to $T_c$. Finally, the condensation of charged bosons in magnetic field is also expected to lead to a positive curvature[21]. But, one has then to take into account the fact that we do not observe any feature in the tunneling spectra above $T_{Cp}$ in zero magnetic field. On the other hand, a second scenario is that $H_{c2} \sim H_\Delta$ and that the specific heat anomaly marks a transition within the vortex state. For instance, specific heat anomalies, both peaks and/or steps, have been observed for transitions in the vortex state in YBCO[22][23]. However, even though the amplitude of $\Delta C_p$ per unit volume measured here is similar to the one associated with vortex melting in YBCO, its shape is quite different and looks much like a classical superconducting transition.

In summary, specific heat and reversible magnetization measurements demonstrate the very peculiar nature of the thermodynamic superconducting transition in the cubic $(K, Ba)BiO_3$ system. The strong deviations from the Ginzburg–Landau model in the reversible magnetiza-
tion, the rapid collapse of the specific heat anomaly with magnetic field and the positive curvature in $H_{cg}(T)$ associated with a vortex-glass scaling behaviour, all suggest the presence of strong fluctuations. It is interesting to note that the superconducting transition in (K,Ba)BiO$_3$ occurs in the vicinity of a metal - insulator transition and the carrier density is very small in this system. This might lead to the presence of large quantum fluctuations. The field $H_\Delta$ for which the superconducting gap completely disappears in tunneling spectroscopy is larger than the field $H_{CP}$ corresponding to the onset of the specific heat anomaly. $H_{CP}$ (as well as any characteristic field deduced from transport measurements) presents a clear positive curvature.

![Temperature dependence of $\partial M_{rev}/\partial \ln(H)$ in a (K,Ba)BiO$_3$ single crystal.](image)

**FIG. 4.** Temperature dependence of $\partial M_{rev}/\partial \ln(H)$ in a (K,Ba)BiO$_3$ single crystal. The dotted line is a WHH fit for the temperature dependence of $1/\lambda^2$ (see text for details). The solid line is a $(1 - T/T_c)^{1.5}$ fit to the data.

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