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Positive curvature in the temperature dependence of H_{c2} in $K_xBa_{1-x}BiO_3$

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We report an upward curvature in the temperature dependence of the upper critical field $H_{c2}(T)$ in $K_xBa_{1-x}BiO_3$ single crystals using ac-susceptibility measurements and magnetic fields up to 25 T. A possible role of Landau quantization in such uncommon behavior is discussed. [S0163-1829(96)03034-2]

The theory by Werthamer-Helfand-Hohenberg[1] (WHH) predicts the universal behavior of the upper critical field $H_{c2}(T)$ in superconductors with weak electron-phonon coupling. The behavior can be described by a universal function $h_{c2}(T)$ expressed in the reduced variables for magnetic field $h=H[T_c(-dH_{c2}/dT)_{T=T_c}]^{-1}$ and temperature $t=T/T_c$. The function $h_{c2}(t)$ has a negative second derivative and saturates to the value $h_{c2}\approx 0.7$ at $t=0$. The WHH theory has described successfully properties of conventional superconductors but many new superconductors discovered during the last decade exhibit behavior inconsistent with the theory. Amorphous alloys based on transition metals[2] and K_3C_{60} (Ref. 3) shows the linear dependence $H_{c2}(T)$ down to low temperatures. Some organic superconductors[4] and electron-doped high-temperature superconductors [$L_{2-x}Ce_xCuO_{4-y}$ where $L=$Pr,Sm,Nd (Refs. 5 and 6)] even have a positive second derivative. Furthermore, in stark contrast to WHH a diverging $H_{c2}(T)$ was observed in overdoped $Tl_2Ba_2CuO_6$ films,[7] where H_{c2} increased rapidly with decreasing temperature in the whole temperature range $1>t>0.001$, and in $Bi_2Sr_2CuO_y$ films.[8]

In this work we report a non-WHH behavior with a positive second derivative in $K_xBa_{1-x}BiO_3$ single crystals. This material represents the family of high-temperature superconductors but is copper-free and has the cubic structure. It has the highest transition temperature among all known copper-free superconductors. At the same time, the upper critical field of $K_xBa_{1-x}BiO_3$ is only about 25 T at helium temperature and this allows detailed measurements of the whole $H(T)$ diagram. There have already been a number of studies of its $H_{c2}(T)$ dependence in relatively low magnetic fields.[9–14] Recently, Affronte *et al.*[15] have extended the earlier work to higher fields and found (using resistance measurements) that $H_{c2}(T)$ dependence has an upward curvature with no sign of saturation down to $T=0.1T_c$. As this contradicts to the conventional WHH theory, the authors expressed some doubts concerning the homogeneity of their samples and the presence of two superconducting phases.[15] We have employed a different experimental technique for tracing the superconducting transition (ac susceptibility) which responds differently if a minor part of the second superconducting phase would be present. Our observation of the upward curvature, when using a different method and samples grown by a different technique, indicates that the violation of the WHH theory is an intrinsic property of $K_xBa_{1-x}BiO_3$ material.

Experimental samples were prepared by electrochemical crystallization.[16] A melted mixture of KOH, $Ba(OH)_2 8H_2O$, and Bi_2O_3 with the ion ratio K:Ba:Bi $=72:1:2$ was kept in an electrolitic bath at 300 °C. The process of crystal growth continued for 3 h and was followed by 20 h of keeping the grown crystals in the melt at the same temperature but without electric current. In the present experiment we have employed two samples which have irregular shape and masses 2.2 and 1.5 mg. They were black in color with a blue shimmer. The critical temperatures of 31.8 and 30.3 K were detected. The superconducting transitions in zero field had widths 1.7 and 2.5 K, respectively. Experimental results were practically identical for both samples and for brevity we present here only those obtained for the sample with the highest T_c.

ac susceptibility of $K_xBa_{1-x}BiO_3$ single crystals has been measured using the standard four-coil compensation scheme. Measurements in fields up to 8 T were carried out in a superconducting solenoid and a Bitter magnet was employed for higher fields up to 25 T. Figure 1 shows experimental curves of the real part of ac susceptibility $\chi'(T)$ versus temperature at fixed values of the magnetic field. The onset of the χ' signal has been taken as the indication of the superconducting transition. Such a convention has been discussed in many of the cited papers and in fields below 10 T it is known to lead to the same $H_{c2}(T)$ dependence as any other method. Furthermore, the fact of the upward curvature for $H_{c2}(T)$ is beyond the uncertainty related to the definition of the superconducting transition on our χ' curves.

The resulting $H(T)$ diagram of $K_xBa_{1-x}BiO_3$ is shown in Fig. 2. The point at the highest field in this plot (solid circle) was obtained using another method. The sample was mounted in a torque magnetometer which measured the force exerted on a magnetic moment by a nonparallel magnetic field or a field gradient. We used the following procedure to detect the superconducting state. The sample (immersed in the exchange gas) was cooled down from a temperature above T_c to 4.2 K in the field 18 T. Then, at the constant temperature of 4.2 K the field was swept up at a constant

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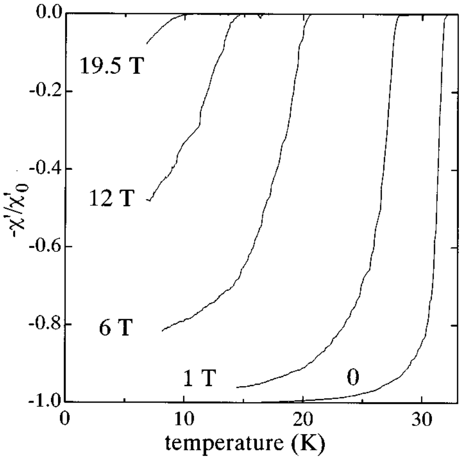

FIG. 1. Real part of ac susceptibility of a $K_xBa_{1-x}BiO_3$ single crystal in various magnetic fields. The measuring frequency is 200 kHz. $\chi'_0=\chi'$ $(T=0,H=0)$.

rate. The measured force increased first linearly with the field indicating the superconducting state with pinned or partly pinned vortices. Then, in the field of 23.7 T we have observed a kink followed by an approximately constant value of the force. Details may be interpreted in different ways but the behavior indicates unambiguously that the superconductivity persists below 23.7 T. We assume this value to be the lower limit for H_{c2} at 4.2 K as indicated by the arrow in Fig. 2.

It is clearly seen from Fig. 2 that $H_{c2}(T)$ in $K_xBa_{1-x}BiO_3$ has a *superlinear* dependence down to $t=0.12$ without any tendency to saturation. The experimental data can be described by the quadratic function (solid line in Fig. 2)

$$H=32.2-1.8T+0.025T^2, \tag{1}$$

where H in T and T in K. The WHH behavior is shown by the dotted curve. The WHH theory requires only the knowledge of values of T_c and $(dH_{c2}/dT)_{T=T_c}$ and the dotted curve represents the best fit to a part of the experimental curve near T_c. The observation of the superlinear dependence may be considered as the main experimental result of this communication. We note that the observed behavior is very similar to the one reported by Affronte *et al.*[15] for their ''most metallic samples.''

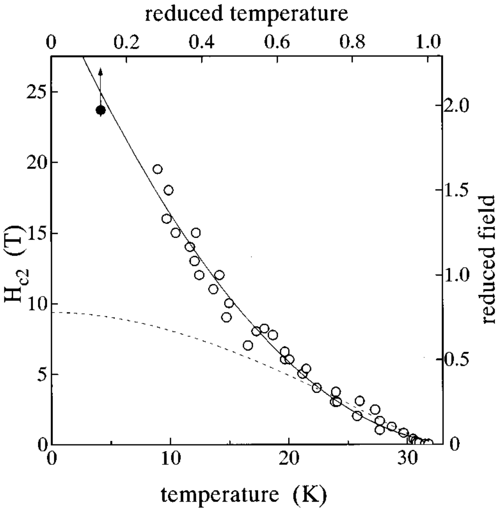

FIG. 2. Temperature dependence of the upper critical field in $K_xBa_{1-x}BiO_3$. The solid circle is the lower limit for H_{c2} at 4.2 K. The solid line is quadratic function (1). The dashed line is the function $h_{c2}(t)$ which follows from the WHH theory. The right scale is normalized to the value $T_c(-dH_{c2}/dT)_{T=T_c}$ which is used as a parameter in the function $h_{c2}(t)$.

There are a number of reasons which may lead to the violation of the WHH theory. They were frequently discussed earlier (see, e.g., Ref. 3) but neither of them is applicable to the case of $K_xBa_{1-x}BiO_3$. For instance, the presence of magnetic impurities or a strong anisotropy are out of suspicion as $K_xBa_{1-x}BiO_3$ is a nonmagnetic material with the cubic structure and a nearly spherical Fermi surface.[17] Also, strong coupling may in general cause a positive curvature of the curve $H_{c2}(T)$ in the middle temperature range.[18] However, $K_xBa_{1-x}BiO_3$ is believed (on the basis of measurements of its tunneling gap[19,20]) to be a superconductor with weak or intermediate coupling. The theory of Kotliar and Kapitulnik[21] takes into account the disorder and predicts an increase in a value of the reduced upper critical field by a factor of not greater than 1.25. This is considerably less than the increase found in our experiment (see Fig. 2).

In the absence of any present theory which could explain the observed behavior, we discuss below another mechanism which in our opinion could lead to low-temperature deviations from the WHH theory. In the presence of Landau quantization the magnetic field not only suppresses the superconductivity but may also result in its partial enhancement due to an increase in the density of states at the bottom of Landau levels.[22–24] For such enhancement to take place, several rather strict conditions have to be met. First, the Landau splitting $\hbar\Omega$ has to be larger than temperature so that the total number of states in the energy interval T near the Fermi level could be increased significantly in high fields. This means in particular that the ''bare'' value $H_{\mathrm{WHH}}(T=0)$ which is determined in the WHH theory by values of T_c and $(dH_{c2}/dT)_{T=T_c}$, has to be large enough. Our material as well as other high-T_c superconductors are good candidates from this point of view. For $K_xBa_{1-x}BiO_3$, the value of $H_{\mathrm{WHH}}(0)$ is about 10 T (see Fig. 2). The scattering frequency $1/\tau$ has to be also small compared to both the Larmour frequency Ω and temperature T

$$\hbar/\tau \ll \hbar\Omega. \tag{2}$$

Otherwise, the broadening of sharp features in the density of states by scattering would destroy any possible enhancement of superconductivity.

A further limitation is due to Zeeman splitting which leads to two Landau ladders, ϵ_n^- and ϵ_n^+ instead of one. Because of the splitting, the Fermi level ϵ_F can coincides with only one spin-polarized Landau level at any one time. As a result, the density of states increases only for half of electrons which has the privileged spin direction. Even if the effective g factor is precisely equal to 2, Landau levels for opposite spin directions, ϵ_n^- and $\epsilon_{n'}^+$, which cross the Fermi energy simultaneously, have different indices $n = n'$ and electrons at these levels have different spatial dependence of the corresponding wavefunctions. This leads to suppression of electron pairing and superconductivity. However, according to Spivak and Zhou,[25] in the presence of Zeeman splitting the disorder may play an important role and help the pairing of electrons. The disorder gives rise to a random potential $V(\mathbf{r})$ which varies the position of the two Landau ladders relatively the Fermi level. Therefore, there are spatially separated regions in the vicinity of some points $\mathbf{r}_-$ and $\mathbf{r}_+$ where Landau levels with the same n but with opposite spin directions are at the Fermi level:

$$\epsilon_F = \epsilon_n^- + V(\mathbf{r}_-), \quad \epsilon_F = \epsilon_n^+ + V(\mathbf{r}_+). \tag{3}$$

If such regions are found at a distance $|\mathbf{r}_- - \mathbf{r}_+|$ smaller than the coherence length ξ_0, superconducting droplets of the size ξ_0 appear. The number of the droplets is determined by a probability of finding such favorable regions at a given random potential $V(\mathbf{r})$.

The pairing condition (3) can be satisfied in some regions at any magnetic field. When the field is changed, the two sets of points, $\mathbf{r}_-$ and $\mathbf{r}_+$, move in space and so do the superconducting droplets. In this model there are no preferable values of the magnetic field and this rules out any Shubnikov–de-Haas-like oscillations in $T_{c2}(T)$ or other thermodynamics quantities which could be expected in the ideal case.[23,26] On the other hand, the enhanced superconductivity is not homogeneous: it exists inside some cluster which volume and specific pattern both depend on the field. The superconducting volume is expected to decrease with increasing magnetic field, in agreement with the behavior in Fig. 1 where the magnetic moment χ' saturates at low temperatures to decreasingly lower absolute values as the magnetic field increases. The increase in H_{c2} due to disorder is compensated by the decrease in the bulk superconducting response.

The discussed model contains two opposing requirements for the disorder. On the one hand, to maintain the increase in the density of states, inequality (2) should be valid. On the other hand, fluctuations of the random potential on the ξ_0 scale should be larger than Zeeman splitting. It is easier to meet these two requirements if the disorder potential $V(\mathbf{r})$ is dominated by relatively long-range fluctuations: the scattering is not so effective in this case. Again, high-T_c superconductors are good candidates for having such type of random potential. Their carrier density depends on the doping level which cannot fluctuate on a very short range. At the same time, fluctuations of the carrier density on the scale of the order of ξ_0 are expected even in high-quality scale crystals. In our samples, the potassium concentration is likely to be such slightly fluctuating parameter which determines the random potential $V(\mathbf{r})$.

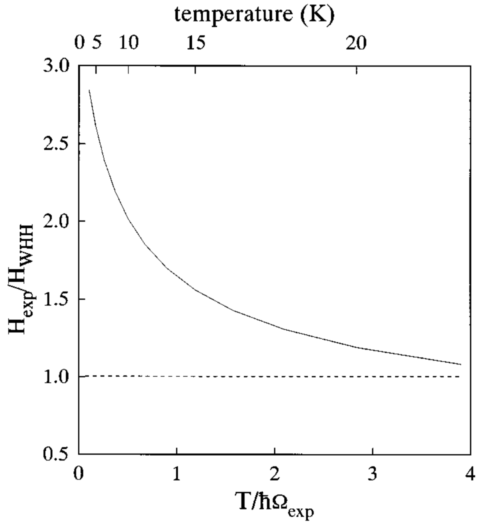

FIG. 3. Enhancement of H_{c2} vs the ratio of temperature to Landau splitting.

If the speculation about the quantization enhancement of the superconductivity is valid, the ratio $T/\hbar\Omega$ is expected to be the major parameter which determines enhancement of the upper critical field. Figure 3 presents our experimental data in the corresponding form. Here, the enhancement of the upper critical field H_{c2} (compared to the value H_{WHH}) is plotted against $T/\hbar\Omega$. The Larmour frequency Ω was calculated from the measured H_{c2} using the free-electron mass. For simplicity, the experimental dependence $H_{c2}(T)$ is taken in the form (1). The obtained function has quite a sensible form from the point of view of the discussed physics: when the parameter $T/\hbar\Omega$ reaches 1 there is a reasonable enhancement of $H_{c2}(T)$ by a factor of about 1.5. The tendency of the function of Fig. 3 to diverge when the argument tends to zero corresponds remarkably to what one could expect within the framework of models.[23,25] Unfortunately, Refs. 23 and 25 do not give any expression for $H_{c2}(T)$ to compare it with our experimental curve.

The discussed model can also explain a qualitative observation of Affronte *et al.*[15] that H_{c2} at low temperatures depends on the crystal quality. While their ‘‘most metallic samples’’ had the upper critical field H_{c2} of about 25 T at 2 K, a sample with 15 times larger resistivity in the normal state remained superconducting, at least partly, up to 32 T. This is in agreement with our suggestion that the random potential is an important factor effecting the value H_{c2}.

In conclusion, we have found a non-WHH behavior of the superconductivity in $\mathrm{K}_x\mathrm{Ba}_{1-x}\mathrm{BiO}_3$ single crystals and attribute it to the presence of Landau quantization which becomes important in superconductors with a high value of the critical field.

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