Thermodynamics of the Superconducting Phase Transition in Ba$_{0.6}$K$_{0.4}$BiO$_3$

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We suggest that the transition to superconductivity in a single crystal of Ba$_{0.6}$K$_{0.4}$BiO$_3$ with a $T_c = 32$K, and having critical fields with anomalous temperature dependencies and vanishing discontinuities in specific heat and magnetic susceptibility, may well be an example of a fourth order (in Ehrenfest’s sense) phase transition. We have derived a free energy functional for a fourth order transition and calculated (for the temperature range $T_c/2 < T \simeq T_c$) the temperature dependence of the critical fields. We find

\[ H_{c1}(T) \propto (1 - T/T_c)^2, \quad H_{c0}(T) \propto (1 - T/T_c)^3 \quad \text{and} \quad H_{c2}(T) \propto (1 - T/T_c)^1 \]

in general agreement with experiments.

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In the Ehrenfest classification of phase transitions, an $n^{th}$ order transition is described by continuous derivatives, with respect to temperature and a mechanical variable (for example a magnetic field or pressure) up to order $(n-1)$. The $n^{th}$ order derivatives are discontinuous. So far however, only first and second order transitions have been observed. There are no known examples of transitions higher in order than two.

We report below, what appears to be an example of a fourth order phase transition. In the course of measuring the magnetization of superconducting Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO), as a function of magnetic field (up to 27T) and temperature (1.3K to 350K) we were surprised to find no evidence of a discontinuity in the magnetic susceptibility. While this was an anomalous property, it was congruent with the other mystery about BKBO, that there is no discontinuity in specific heat either at $T_c$, at $T_c$, that is $\kappa$ at $T_c$, that is, we find experimentally that the lower critical field, $H_{\text{lc}}(T)$, is given by $0 < H < H_{\text{lc}}$.

$\chi(T)$ is a function of magnetic field and temperature. We see that in the common thermodynamic observables, $\Delta C(T)$, $\chi(T)$ vanishing, a question arises concerning the order of this transition. The answer is provided by the thermodynamic critical field $H_0(T)$. Since in the superconducting state, the thermodynamic critical field, $H_0(T)$, is given by

$F(T) = -H_0^2/8\pi$. This is the free energy of the superconducting state that is derived from the experimentally determined $\chi(T)$, thus, in case of a second order phase transition, should have the temperature dependence $F(T) = -H_0^2/8\pi \propto -(1-T/T_c)^2$. That is, $H_0(T)$ would be linear in $(1-T/T_c)$, apart from critical fluctuation effects which lead to a divergent specific heat. As shown in Fig. 1 with $T_c = 32 K H_0(T) \propto (1-T/T_c)^2$. Since for an $n^{th}$ order phase transition, the critical field has an exponent of $n/2$, the transition here must be of fourth order in the sense of Ehrenfest.

Further support for this assertion comes from the temperature dependence of other critical fields. In particular, we find experimentally that the lower critical field, the field which separates the Meissner state (no flux in the sample) from the Abrikosov state (partial flux penetration in the form of a vortex lattice), depends on temperature as $H_0^2(T) \propto (1-T/T_c)^2$. As shown in Fig. 2. The upper critical field, which separates the Meissner state from the normal state is measured to be $H_{\text{cu}}(T) \propto (1-T/T_c)^{1.2}$ as shown in Fig. 3. The upper critical field, which separates the Abrikosov state from the normal state is measured to be $H_{\text{cu}}(T) \propto (1-T/T_c)^{1.2}$ as shown in Fig. 3. This fact leads to an anomalous result, specific to this higher order phase transition. For a BCS superconductor, the ratio $\kappa^2 = H_{\text{cu}}(T)/H_{\text{cu}}(T)$ is a constant. Here it diverges approximately as $(1-T/T_c)^{-2}$. Both of the critical fields are inversely proportional to squares of the two length scales in the problem, the London penetration length $\lambda$, which controls the flux penetration and therefore the size of a vortex, and the superconducting coherence length $\xi$ which determines the stiffness of the local density of the superconducting electrons. In a BCS superconductor, these length scales are identical in their temperature dependence. To our knowledge there is no fundamental reason why $\kappa$ should be a constant.

In the following we derive a free energy functional which describes the properties of a fourth order phase transition. Once we include the interaction of the superconductor with the magnetic field in the usual gauge invariant form, we also can derive the temperature dependencies of the critical fields. These results are in full accord with the experiments.

The free energy is derived following the requirement of a fourth order phase transition, viz. $F(T) = -f_c(1-T/T_c)^4$ as a function of temperature. The free energy is in the spirit of a Ginzburg-Landau (GL) functional which is minimized with respect to the complex order parameter $\psi = \Delta e^{i\phi}$. The value at the minimum then is the thermodynamic free energy. The first two terms are self evident. Indeed it is important that the terms proportional to $|\psi|^2$ and $|\psi|^4$ be not present. The form of the spatial gradient term is also determined by the same considerations. The term below is the one with the lowest power of gradients. Higher power of gradients such as $|\psi|^2$ and $|\psi|^4$ are possible but they contribute higher order nonlinear contributions of the magnetic field and therefore are unnecessary for a stability analysis. They can be included for effects nonlinear in the magnetic field. The free energy functional appears as,

$$F_{IV}(\psi, T) = a|\psi|^6 + b|\psi|^8 + c|\psi|^2\nabla|\psi|^2$$

Here $a = a_o(T/T_c - 1)$ and $b$ and $c$ are positive constants.

The minimum of this free energy corresponds to an order parameter amplitude $\Delta(T) \propto (1-T/T_c)^{1/2}$. The specific heat is expected to be $C_V(T) \propto (1-T/T_c)^2$, and $\chi = \frac{d\Delta}{dT} \propto (1-H/H_0)^2$. The thermodynamic discontinuities are in the fourth derivative of the free energy (or in the second derivative of specific heat as a function of temperature or the second derivative of the magnetic susceptibility $\chi$ with respect to the magnetic field). We see that in the common thermodynamic observables, there are no discontinuities, as seen in the experiments.

It is conceivable that broad transitions that have been observed in the past, instead of being recognized as candidates for a higher order phase transition were forcibly squeezed into a second order framework. The Ehrenfest relation appropriate for a IV order phase transition is

$$\left(\frac{dH}{dT}\right)^4 = \frac{\Delta^2}{T_c}\frac{\xi a}{\phi_o A}$$

In the presence of a magnetic field the gradient term transforms as $\nabla \to (\nabla + \frac{2\pi}{\phi_o} A)$, where $A$ is the vector
potential. Here \( \phi_0 \) is the flux quantum, \( \phi_0 = h/2e = 2 \times 10^{-15} \text{T-m}^2 \). Thus Eq. (2), as always, is the basis for a study of both spatial thermodynamic fluctuations as well as magnetic field effects. We note that the penetration depth for a magnetic field, the coefficient of the \( A^2 \) in the generalized Eq. (2), diverges as

\[
\lambda^{-2}(T) = \frac{4(2\pi)^3}{\phi_0^2} e \Delta^6 \propto (1 - T/T_c)^3
\]  

(4)

This too is in agreement with experiments, not as a direct measurement but that of \( H_c(1) \propto \phi_0/A^2 \). This is shown in Fig. 3 with \( H_c(1) \) plotted as a function of temperature. Here the data on the lower critical field is limited by its size at temperatures close to \( T_c \). At low temperatures (less than \( T_c/2 \)), \( H_c(1) \) behaves linear in \( T \) and has the right intercept at \( T_c \). The spatial fluctuations of the order parameter are still governed by \( \xi^2 = c/a \cdot (1 - T/T_c)^{-1} \). For \( H_{c2}(T) \) we recognize that \( \phi_0/\xi^3 = H_{c2}(T) \). Experimentally, as shown in Fig. 3, the exponent is nearly one.

The proposal here rests on several critical assumptions. For example, Graebner et al. have reported a very small specific heat discontinuity. The reported discontinuity is in fact anomalously small and roughly of the size of their experimental uncertainty. To estimate the expected discontinuity, consider the specific heat results in ref [9]. The high temperature limit of the specific heat can be described by \( C(T) = \gamma T + \beta T^2 \) with \( \gamma \approx 150 \text{mJ/moleK} \) as the electronic contribution to \( C(T) \). This large \( \gamma \) puts BKBO in the category of heavy fermion compounds and the expected \( \Delta C \) (of the order of \( \gamma T_c \)) should be nearly 5J/moleK, considerably more (by a factor of 10^5) than the experimental uncertainty and the reported value in ref [9]. Moreover, Hundley et al. find that at low temperatures (\( T < T_c/2 \)), the linear term in \( C(T) \) disappears. The specific heat then is given by \( C = \beta T^3 \), where \( \beta > \beta_c \). But this larger \( \beta \) may well be due to the presence of nodes in the putative energy gap at the Fermi surface. For example point nodes in the energy gap give rise to a \( C \propto T^3 \) as the well known phonon contribution with the same power.

Another basis for the suggestion here is the temperature dependence of the lower critical field \( H_{c1}(T) \). The cubic temperature dependence of the lower critical field \( H_{c1}(T) \) is linear, as expected for a second order BCS superconductor. However, closer inspection reveals that the \( H_{c1}(T) \) values of Hall et al. (the values used in this analysis) are at low temperatures \( T < T_c/2 \) in agreement with the results of Graebner et al. who employed in their study high quality microcrystals to eliminate spurious effects associated with sample inhomogeneities. The values given in ref [9] for \( T > T_c/2 \) can be seen to follow a straight line but extrapolate to a smaller \( T_c \approx 27 \text{K} \). When the zero field \( T_c \approx 32 \text{K} \) is included, it is impossible to avoid a curvature in the temperature dependence of \( H_{c1}(T) \).

We note, in passing, that the relation \( H_{c2}^2 = H_{c1}H_{c2} \) is still valid. The consequences, near \( T_c \), of a divergent \( \lambda \) are more curious. For example the central result that the flux expulsion happens more slowly in the mixed state is clear. That the vortex lattice appears more slowly and therefore the irreversibility field is smaller is less obvious. Other questions such as the symmetry of the vortex lattice are currently under study and will be reported later. Similarly, the surface energy of a normal-superconducting (N-S) domain wall, is negative and proportional to \( \lambda \) and therefore larger than in a BCS case. It may well engender a more inhomogeneous ground state at \( H_{c2} \). A numerical analysis of these questions is in progress and will be reported later.

It is important to note that the thermodynamic behavior changes for \( T \leq T_c/2 \). This is clearly seen in several independent measurements, for example specific heat and critical fields. The discussion here is focussed on the order of the transition from the normal state and is therefore limited to the vicinity of \( T_c \). However, a microscopic theory which might attempt to derive Eq. (2) will also have to include an explanation of this crossover behavior and possible existence of point nodes in the energy gap.

It might also contain an explanation of why the free energy does not contain terms such as \( \Psi^2 \) and \( \Psi^4 \). Presently, we can only speculate about a microscopic theory. In a sense, this question is equivalent to the seemingly deeper question: Why is the transition of order IV? In this paper, we have focussed on the properties of a IV order phase transition, but let’s speculate: for instance, the BCS/GL theory contains an overall factor of density of states at the Fermi surface. Suppose, as discussed in ref. [9], the density of states \( N(0) = 0 \) for \( T \geq T_c \) and \( N(0) \propto \Psi^2p \) for \( T \leq T_c \). This would be a transition from an insulator to a superconductor, the free energy for \( p = 1 \) would not have a \( \Psi^2 \) term and the order of the transition would be III. For \( p = 2 \), the transition would be of order IV.

Now, addressing the relationship between fluctuations as developed for a II order phase transition and the framework: in a second order phase transition, including the critical effects, one might view the free energy as depending on temperature as \( F_o(T) = -f_o(1 - T/T_c)^{(2 - \alpha)} \) Thus the small quantity \( \alpha \) is calculated by pseudo-perturbative schemes (such as Gaussian approximation or some version of renormalization group). It is clear, however, that a value of \( \alpha = -1 \) or \(-2 \) is essentially beyond the realm of a perturbative approach. If the free energy exponent is significantly different from 2, then the unperturbed ground state could be a transition of order corresponding to the nearest integer, about which a calculation of fluctuations could be done in the future.

The conclusions presented here are the first part of a
work in progress. We are currently working on determining (1) the magnitude of the fluctuations, and (2) whether there is an upper critical dimension and, if so, what it is. These, and other points of interest, will be presented in forthcoming publications.

In summary then, we have analyzed the thermodynamic properties of the superconducting phase transition in Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO). The absence of a discontinuity in specific heat and magnetic susceptibility, on transforming from the normal to superconducting state, shows that the phase transition cannot be of second order. The temperature dependence of the thermodynamic critical field shows that the transition is fourth order. The conclusions about other critical fields, derived from a free energy developed for a fourth order phase transition, i.e. $H_{c1}(T) \propto (1 - T/T_c)^3$ and $H_{c2}(T) \propto (1 - T/T_c)$ are in accord with the experiments.

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FIG. 1. The values of the thermodynamic critical field $H_0$ are plotted here as a function of $1 - T/T_c$. $H_0(T) = 0.509 \cdot (1 - T/T_c)^{1.807 \pm 0.052}$ tesla with $T_c = 32$ K.
FIG. 2. The lower critical field $H_{c1}$ is plotted as a function of $1 - T/T_c$. $H_{c1}(T) = 0.0955 \cdot (1 - T/T_c)^{3.027\pm0.156}$ tesla with $T_c = 32$ K. Below roughly $T = T_c/2$ the data is approximately linear.
FIG. 3. Shown here is the upper critical field $H_{c2}$ plotted as a function of $1 - T/T_c$. $H_{c2}(T) = 0.00197 \cdot (1 - T/T_c)^{1.213 \pm 0.021}$ tesla with $T_c = 32$ K.