Magnetic flux motion and flux pinning in superconductors

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Magnetic flux motion and flux pinning in superconductors

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by

Steven C. Sanders

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CHAPTER 1. INTRODUCTION

The goal of this research is to study the transformation from reversible to irreversible magnetic behavior in the high-$T_c$ superconductors Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ and Ba$_{0.6}$K$_{0.4}$BiO$_3$ and compare the results with other high-$T_c$ superconductors. This chapter will begin with a brief survey of some historical highlights in the understanding of superconductors, followed by a discussion of the magnetic properties of conventional type-I and type-II superconductors. The remaining part of the chapter will review some of the properties of the high-$T_c$ superconductors, emphasizing the differences observed in the field-temperature ($H$-$T$) phase diagram compared to conventional superconductors.

1.1. Conventional (Low-$T_c$) Superconductors

The study of superconductivity began in 1911 with the discovery of a sudden loss of electrical resistance in mercury at $T_c = 4$ K [Onnes, 1911]. The critical transition temperature $T_c$ is the temperature below which dc resistance vanishes (perfect conductivity) and magnetic flux is expelled from the interior of the sample (perfect diamagnetism). The latter phenomenon, known as the Meissner effect [Meissner, 1933], is observed when cooling the superconductor from above $T_c$ to below $T_c$ in the presence of a suitable magnetic field. The Meissner effect is the unique signature of superconductivity, since perfect conductivity would imply only that the sample should trap flux inside the sample when cooling through $T_c$, not expel it completely. The Meissner effect also implies that superconductivity can be destroyed by a sufficiently large magnetic field, the thermodynamic critical field $H_c$. The critical field $H_c$ is related thermodynamically to the free-energy difference between the normal state and superconducting state in zero field, which is also known as the condensation energy of the superconducting state. In zero field, the transition
from the normal state to the superconducting state is a second order phase transition with a
jump in specific heat, but no latent heat; with a field present the transition is first-order
[Rose-Innes, 1978].

Based on thermodynamics, Gorter and Casimir [Gorter and Casimir, 1934] used a
two-fluid model to explain many properties of superconductors. In this model, the
conduction electrons below $T_c$ are divided into two classes, superelectrons having zero
resistance and normal electrons behaving like conduction electrons in a normal metal. The
relative electron density in the two fluids depends on the temperature. This model is still
useful today when discussing the temperature-dependence of the penetration depth $\lambda(T)$.

The two basic electrodynamic properties, perfect conductivity and the Meissner
effect, were described by a phenomenological model developed in 1935 [London and
London, 1935]. This model introduced a penetration depth $\lambda_L$ to describe the characteristic
length over which magnetic flux is exponentially screened from the sample by supercurrents
in the presence of a weak field. The main drawback of this model is that it is local in nature,
and so it is only applicable for materials with a short mean-free path.

A non-local generalization of the London equations was proposed by Pippard
[Pippard, 1953]. The main contribution was the introduction of a coherence distance $\xi_0$, a
characteristic dimension of the superconducting wavefunction which accounts for the long-
range interaction of the electrons.

The Ginzburg-Landau (GL) theory [Ginzburg and Landau, 1950] describes the
macroscopic electrodynamic response of the superfluid to externally-applied fields and
currents. GL theory accommodates the strong fields and spatial inhomogeneities that the
London model cannot. A complex order parameter $\Psi$ is introduced for the superconducting
electrons, and $\Psi$ is normalized such that the local density of Cooper pairs (from BCS theory,
below) \( n_s(r) = |\Psi(r)|^2 \). This order parameter is analogous to the single-particle wavefunction in quantum mechanics in that it can be thought of as the wavefunction of the center-of-mass motion of the Cooper pairs [Tinkham, 1975]. The GL theory starts with the Helmholtz free energy density expanded in terms of \( \Psi \) and \( \nabla \Psi \) and uses a variational principle to derive two differential equations, the GL equations. From these equations, the GL coherence length \( \xi(T) \) can be obtained. This is the characteristic length over which the order parameter can spatially vary. The dimensionless GL parameter \( \kappa = \lambda / \xi \) is quite useful in characterizing different types of superconductors, as will be discussed below. The GL theory is only strictly valid very near \( T_c \), but it can often be applied at lower temperatures with only a small error.

The Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity [Bardeen, Cooper, and Schrieffer, 1957] is a microscopic quantum theory which describes a number of observed superconducting phenomena. In particular, it predicted the existence of an energy gap between the superconducting ground state and the quasiparticle excitations of the system. The BCS theory showed that the superconducting charge carriers were comprised of pairs of electrons, called Cooper pairs, which have which have equal and opposite momentum and spin. These pairs have spatial extension of order \( \xi_o \), and are formed by a weak attractive interaction between electrons caused by the electron-phonon interaction. This theory did not account for the spatial variation of the superconducting wavefunction in space; the GL equations do permit this variation and are the most useful for treating a wide range of electrodynamic phenomena in superconductors. Gor'kov [Gor'kov, 1959] showed that the GL theory was a limiting form of the (reformulated) microscopic BCS theory, and that the GL order parameter \( \Psi \) is directly proportional to the BCS gap parameter \( \Delta \).

Superconductors are classified according to their magnetic properties as either type-I or type-II depending on the value of their Ginzburg-Landau parameter \( \kappa = \lambda / \xi \). Type-I
superconductors have \( \kappa < 1/\sqrt{2} \), and a magnetization curve for a type-I material is sketched in Fig. 1.1a. As field is increased from zero for a sample below \( T_c \), a magnetic moment is induced by screening currents within a penetration depth of the surface such that the induction \( B \) inside the sample is zero. Stated another way, the magnetization \( 4\pi M \) is equal and opposite to the internal field \( H \), since \( B = 4\pi M + H \). This perfect diamagnetism continues until the field value reaches the critical field \( H_c \), at which time the material loses its superconductivity and becomes normal. If the sample were initially at a temperature above \( T_c \) in the presence of a magnetic field \( H < H_c \) and were subsequently cooled below \( T_c \), then all magnetic flux would be expelled due to the Meissner effect. The phase diagram in the \( H-T \) plane for a type-I superconductor is shown in Fig. 1.2a. There are only two possibilities, either a superconducting Meissner state below \( H_c(T) \), or the non-superconducting normal state above \( H_c(T) \).

Abrikosov first predicted the existence of type-II superconductors in 1957 [Abrikosov, 1957]. Starting from the Ginzburg-Landau theory, he showed that for large values of \( \kappa \) (\( \kappa > 1/\sqrt{2} \)), a negative surface energy should be expected at the interface between a superconductor and normal region. To minimize free energy, subdivision of the superconductor into domains of normal material should occur for certain field values. Abrikosov showed that two critical fields, \( H_{c1} \) and \( H_{c2} \), exist for type-II superconductors. For fields smaller than \( H_{c1}(T) \), the superconductor is in the Meissner state (as a type-I material would be for fields smaller than \( H_c \)), and for fields larger than \( H_{c2}(T) \), the sample is in the normal state. For \( H_{c1} < H < H_{c2} \), the superconductor is in the mixed (or Abrikosov) state, where magnetic flux enters into the sample in the form of quantized flux lines, or vortices, with each line having one quantum (\( \Phi_0 = hc/2e \)) of magnetic flux. The local flux density of each line extends approximately a distance \( \lambda(T) \) from the center of the line. The circulating current which forms the flux line also extends a distance \( \lambda(T) \) from the line.
Fig. 1.1 Magnetization-versus-field curves for: (a) type-I superconductor, (b) ideal (non-pinning) type-II superconductor, and (c) non-ideal type-II superconductor
Fig. 1.2 Field-temperature phase diagrams for (a) type-I and (b) type-II superconductor
center. At the center of each flux line is normal core where the order parameter \(|\Psi|\) goes to zero over a distance on the order of the coherence length \(\xi(T)\). This is sketched in Fig. 1.3a. The flux lines, which lie along the direction of the applied field, repel each other, and in an ideal type-II superconductor (one with no pinning by defects) the lines form a triangular lattice, as illustrated in Fig. 1.3b. The magnetization curve for an ideal type-II superconductor is shown in Fig. 1.1b, and the phase diagram appears in Fig. 1.2b. Perfect diamagnetism exists up to \(H_{c1}(T)\), at which time the sample enters the mixed state, where flux lines penetrate the bulk of the sample and perfect diamagnetism no longer exists. \(H_{c2}(T)\) is the field at which vortices are first nucleated upon cooling from above \(T_c\). The magnetization curve is reversible for an ideal superconductor.

Inhomogeneities always exist in real superconducting materials. In the mixed state the flux lines interact with the inhomogeneities and may become pinned, that is, as the applied field is removed, magnetic flux may remain in the sample. This results in hysteresis of the magnetization curve rather than the reversible magnetization of an ideal material. A hysteretic magnetization curve is sketched in Fig. 1.1c.

Non-ideal type-II superconductors are the most attractive materials for high-field and high-current applications. Type-I superconductors typically have critical field values too low for practical applications. Passing even a modest current through a wire made of a type-I superconductors could result in a field exceeding \(H_c\), thereby driving the material normal. Type-II superconductors remain superconducting up to \(H_{c2}\), which can be much larger than the \(H_c\) of both types. In an ideal type-II superconductor, however, fields larger than \(H_{c1}\) would nucleate vortices in the bulk of the sample, and these vortices would move under the action of a Lorentz force from an external current, resisted only by a viscous drag [Bardeen and Stephen, 1965]. This flux motion would create a voltage (from Faraday's law), and the desired zero resistance would be lost. With defects to pin the flux lines, however, there is
Fig. 1.3  (a) Behavior of magnetic flux density and order parameter for an isolated vortex. (b) Triangular Abrikosov vortex lattice
zero resistance as long as the Lorentz force does not exceed the pinning force. The maximum current which does not depin the flux lines is called the critical current. Since the type and density of defects can be varied by different fabrication processes, the value of the critical current density depends on the preparation method. Hence, unlike the critical transition temperature or the critical fields, the critical current density is an extrinsic quantity that is determined mainly by the flux pinning strength of the material [Dew-Hughes, 1971; Campbell and Evetts, 1972].

The Bean model [Bean, 1962, 1964] was the first model to successfully explain the irreversible magnetization and its relation to the critical current density. As the applied field is increased above $H_{c1}$, flux enters the sample, but the pinning sites hold the flux near the surface, causing a flux density gradient. As the field is increased, flux penetrates farther into the sample, but a gradient still exists. By Ampere's law $\nabla \times \mathbf{H} = 4\pi \mathbf{J}$ the gradient produces a current perpendicular to the field. According to the Bean model, the effect of pinning determines only a maximum flux density gradient supported by the pins and therefore a maximum critical current. A critical state is established as long as the critical current density is equal to the gradient of local flux density in the sample.

The pinning of the magnetic flux prevents an equilibrium flux distribution from being realized. This means that at a point on an irreversible magnetization curve the critical state is a metastable state, not an equilibrium state. Even with strong pinning, the resistance is not actually zero, according to the flux creep model [Anderson, 1962]; thermal energy can excite flux over a pinning barrier to the next pinning site. In conventional superconductors, however, this creep rate is extremely small. A logarithmic decay in the magnetization due to thermally activated flux creep was observed by Kim et al. [Kim et al., 1962] in NbZr tubes. These samples showed a decrease in the trapped flux at a rate of about 5 G per decade of time (starting with a trapped field of 4000 G). Extrapolating this logarithmic decay, it can be
shown that the persistent current would require \(10^{300}\) years to decay to zero [Tinkham, 1975]. Superconducting magnets are operated rather far from the critical state, so the flux leakage is made even smaller.

1.2. High-\(T_c\) Superconductors

In the seventy-five years following Onnes's discovery of superconductivity in 1911, superconductivity was observed in thousands of materials, but the largest observed critical transition temperature was only 23 K. In a flurry of activity between 1986 and today, materials having transition temperatures up to 125 K have been discovered and intensely studied. These have come to be known as the high-temperature superconductors (HTSC).

Bednorz and Müller made the initial discovery of high-\(T_c\) superconductivity when they observed a transition temperature of 35 K in \(\text{La}_2\text{Ba}_4\text{CuO}_{4+y}\) [Bednorz and Müller, 1986]. Substituting Sr for Ba in this compound resulted in \(T_c\)'s up to about 40 K [Tarascon et al. 1987; van Dover et al., 1987]. Superconductivity above liquid nitrogen temperature was observed for the first time in \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) (Y123) [Wu et al., 1987], which has a \(T_c\) up to 93 K. The \(\text{Bi-Sr-Ca-Cu-O}\) compounds [Maeda et al., 1988] with \(T_c\) up to 120 K, and the \(\text{Tl-Ba-Ca-Cu-O}\) compound [Sheng and Hermann, 1988] with \(T_c\) up to 125 K were discovered in 1988.

The \(\text{La, Bi, and Tl}\) compounds have tetragonal crystal structures with planes of Cu and O atoms that profoundly affect superconductivity in these materials. The Y123 compound is orthorhombic and has Cu-O chains as well as planes. The Cu-O planes play the major role in generating superconductivity, and lead to the unusually-anisotropic physical properties of these superconductors [Ginsberg, 1989]; the Cu-O chains in Y123 act as electron reservoirs [Tarascon et al., 1988]. The \(\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}\) compound and the Y123
compound have a double Cu-O layer in each unit cell, and the Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O compounds have multiple Cu-O layers, depending on the stoichiometry. Charge transport and superconductivity in these compounds are thought to be due mainly to the holes on the oxygen sublattice in the Cu-O planes [Tranquada et al., 1987; Shen et al., 1987; Nucker et al., 1988].

The high-\(T_c\) cuprates have three distinct characteristics that dramatically affect their observed properties and make them significantly different than the conventional, low-\(T_c\) superconductors: high temperatures, small coherence length, and large anisotropy. The first, and most obvious, is the higher superconducting temperatures. The larger available temperatures, roughly an order of magnitude larger than conventional materials, make thermal activation of flux lines more prevalent and make the lattice contribution in specific heat measurements a larger fraction of the total signal, to give two examples. The second characteristic of high-\(T_c\) cuprates is the short coherence length \(\xi\). In the new superconductors, a representative value of \(\xi\) is on the order of 1 nm, the same order as the unit cell’s dimension, compared to 10-1000 nm in conventional materials. In GL theory, \(\xi\) is the distance over which the order parameter (and hence the density of Cooper pairs) may vary. This makes the superconductor much more sensitive to inhomogeneities such as grain boundaries in polycrystalline samples, which are weak links in HTSC [Ekin et al., 1987]. Dimos et al. [Dimos et al., 1990] showed that the critical current density across a grain boundary in Y123 is 50 times smaller than the critical current density within a grain. In a conventional superconductor such as Nb\(_3\)Sn, grain boundaries are actually desirable as pinning sites, and do not disrupt the supercurrent flow. Increased flux creep is another consequence of a short coherence length (and high \(T_c\)), presumably because the volume of moveable flux is smaller [Yeshurun and Malozemoff, 1988], which leads to a smaller barrier energy in the Anderson model of flux creep [Anderson, 1962]. Fluctuation effects are also
enhanced by a short coherence length, and $H_{c2}$ values are also much larger. The third characteristic of HTSC is the large anisotropy. This can be expressed in terms of an anisotropy parameter $\Gamma$, the ratio of the effective quasi-particle masses in the $c$ and in the $ab$ direction. The anisotropy is reflected in the anisotropy of upper and lower critical fields and the GL coherence lengths $\xi_{ab}$, $\xi_c$, and the penetration depths $\lambda_{ab}$ and $\lambda_c$. The relation is $\Gamma = (\xi_{ab}/\xi_c)^2 = (\lambda_c/\lambda_{ab})^2$. In the Bi(2212) and Tl(2212) compounds, $\Gamma > 3000$ [Farrell et al., 1989] and $\Gamma > 10^5$ [Farrell et al., 1990] have been reported respectively. Y123 is less anisotropic, with $\Gamma > 29$ [Farrell et al., 1988]. This anisotropy parameter is related to the coupling strength between the CuO$_2$ layers in these materials, and for the most anisotropic materials, the conventional flux tube may actually be segmented into two-dimensional pancake vortices [Clem, 1991a] for screening currents in the CuO$_2$ planes.

The three characteristics of HTSC listed above have a large influence on the field-temperature ($H$-$T$) phase diagram of these materials. A generic phase diagram for the high-$T_c$ superconductors is sketched in Fig. 1.4. Although HTSC have some similarities with the conventional type-II superconductors such as the presence of vortices in the Abrikosov phase, and magnetic irreversibility arising from defects and pinning, there are distinct differences, and the magnetic properties of HTSC are much more complicated. The mean-field $H_{c2}(T)$ line is obscured by the presence of fluctuations at the higher temperatures. Within and below this region of strong fluctuations lies a reversible region in which the vortices that were nucleated at $H_{c2}(T)$ on cooling are not pinned, but move reversibly into and out of the sample as field is applied and removed. This reversible region may be thought of as a vortex liquid regime. Pinning of the magnetic flux does not occur until the temperature and field are lowered below the irreversibility crossover $H_{irr}(T)$. Critical currents are not observed above this crossover.
Fig. 1.4  Generic phase diagram in the H-T plane for a high-$T_c$ superconductor
Fluctuations smear out the well-defined $H_{c2}(T)$ line that is observed in conventional superconductors. Traditional methods of mapping the $H_{c2}(T)$ line such as the resistivity transition in a magnetic field and the GL linear extrapolation to $M=0$ in magnetization-temperature curves are no longer effective. A broadening in the magnetoresistance occurs as field is increased [Iye et al., 1987; Sun et al., 1987; Worthington et al., 1988; Worthington et al., 1990; Tinkham, 1988; Palstra et al., 1988a; Palstra et al., 1988b; Palstra et al., 1990].

The standard method of defining $T_c^z = T_c(H=H_{c2})$ as the temperature at which the resistance equals some percentage of the normal state resistance (0, 10, 50, or 90%) resulted in curves which did not coincide [Moodera et al., 1988]. In magnetization measurements, the method of using the Abrikosov result $-\pi M = (H_{c2} - H) / [(2\kappa^2 - 1)\beta]$ to extrapolate the linear portion of the $M$-vs-$T$ curve to $M=0$ has been used by Welp et al. [Welp et al., 1989] to obtain $H_{c2}(T)$. Due to fluctuations, however, there is considerable rounding of the magnetization curves near $T_c$, where the Abrikosov result should be most applicable. As an alternative to the linear extrapolation, Hao and Clem [Hao and Clem, 1991a] have proposed a model based on GL theory. This model applies for lower temperatures than the Abrikosov result. In the case of Y123, the Hao-Clem model gives a $dH_{c2}/dT$ which differs from the value obtained from utilizing the Abrikosov result by about 20% [Hao and Clem, 1991a].

Fluctuations make the determination of $T_c$ much more difficult. In the absence of fields and gradients, the difference in free energy density between the superconducting state and normal state can written as $f_s - f_n = \alpha |\Psi|^2 + \frac{1}{2} \beta |\Psi|^4$, from GL theory. If $\alpha$ is positive, corresponding to the normal state, the free energy minimum occurs when $|\Psi|^2 = 0$. If $\alpha$ is negative, corresponding to the superconducting state, then the minimum free energy occurs when $|\Psi|^2 = |\Psi_s|^2 = -\alpha / \beta$. The result is $f_s - f_n = -\alpha^2 / 2\beta$. $T_c$ is defined as the highest temperature at which $|\Psi|^2 \neq 0$ gives a lower free energy than $|\Psi|^2 = 0$. At this temperature, $\alpha(T)$ changes sign, becoming negative in the superconducting state [Tinkham, 1975].
Thermal fluctuations in the system can change the free energy by an amount \( \sim kT \), however, which leads to the existence of superconducting effects above \( T_c \) and normal-state effects below \( T_c \) [Tinkham, 1975]. Fluctuations cause the finite resistivity below \( T_c \), and diamagnetism above \( T_c \). The magnitude of the fluctuation effects are largest if confined to a small volume. The high-\( T_c \) superconductors, having much smaller coherence volumes than conventional superconductors, exhibit stronger fluctuation effects. Lee et al. [Lee et al., 1988], for example, observed fluctuation-induced diamagnetism up to 200 K in \( \text{Y123} \).

Fluctuation effects also impact specific heat measurements of HTSC near \( T_c \). The behavior of the specific heat jump near \( T_c \) in the presence of a magnetic field is qualitatively different in this material than that observed for conventional superconductors. In conventional materials, the application of a magnetic field causes a large shift of the jump down in temperature, without substantially broadening the jump. In Nb, which is a conventional type-II material, a broadening of only about 10 mK accompanies a shift in the transition of 4 K [Farrant and Gough, 1975]. In the high-\( T_c \) \( \text{Y123} \), however, the application of a magnetic field causes a significant broadening and decrease in amplitude of the jump, but the onset temperature remains constant [Phillips et al., 1987; Salamon et al., 1988; Salamon et al., 1990; Inderhees et al., 1991]. This is interpreted in terms of broadening of the critical regime by the magnetic field. According to Inderhees et al. [Inderhees et al., 1991], this broadening occurs because the field reduces the effective dimensionality from \( d=3 \) to \( d=1 \) [Lee and Shenoy, 1972] as the coherence length perpendicular to the field is limited to the Landau radius \( a_0 = (\Phi_0/2\pi H)^{1/2} \). Inderhees et al. measured the specific heat jump near \( T_c \) in \( \text{Y123} \), and found, in zero field, that the jump could be fit by adding Gaussian fluctuations to a BSC-like step. The field-dependence of the specific heat jump, however, required critical fluctuations for a satisfactory fit [Inderhees et al., 1991].
The irreversibility crossover was first observed in bulk La$_{2-x}$Ba$_x$CuO$_4$ in 1986 [Müller, Takashige, and Bednorz]. In the dc magnetization measurements, a reversible region of finite diamagnetism below $T_c$ and a well-defined onset of irreversible magnetization were observed. They defined the irreversibility point as the temperature where the zero-field cooled (ZFC) and field-cooled (FC) $M$-vs-$T$ (constant $H$) curves split. This transition was found to obey $(1 - T_{irr}/T_c) \approx H^{2/3}$, which led them to suggest that this was a superconducting-glass transition, as this is the same dependence observed for spin glasses. Yeshurun and Malozemoff [Yeshurun and Malozemoff, 1988] observed a similar relationship between $T_{irr}$ and $H$ in the magnetization of a single crystal of Y123. They interpreted this transition based on the conventional flux-creep model [Anderson, 1962; Kim, 1964] and derived this relationship based on a flux-pinning argument. They observed a logarithmic decay of the magnetization with time, as predicted by the Anderson-Kim creep model, and concluded that the pinning potential for Y123 was an order of magnitude lower than for conventional superconductors. Thermal activation was also observed in resistivity experiments [Palstra et al., 1988b; 1989; 1990]. They found that the flux creep resistivity depends exponentially on the temperature as a result of thermally activated processes.

Magnetic decoration experiments provide direct evidence of the unusual behavior of the flux-line lattice in HTSC. Results showed that the Abrikosov lattice was well formed at low temperatures and fields, but at 77 K, no evidence of the lattice was detected [Gammel et al, 1987; 1988; Murray et al., 1990]. This raises the possibility that the lattice might be melted above a certain temperature $T_m$. In a melted flux lattice, flux lines move freely, and there is no significant correlation between lines.

Gammel et al. [Gammel et al., 1988] measured the temperatures of maximum dissipation in Y123 single crystals using a high-Q mechanical oscillator and identified the crossover as the flux-line-lattice melting temperature. Recent experiments using a torsional
oscillator provide rather convincing evidence for flux-lattice melting [Farrell et al., 1991]. Melting temperatures of crystalline flux lattices have been calculated from the elasticity of the flux-line lattice using the anisotropic GL theory [Brandt, 1989; Houghton et al., 1989], while the melting of a disordered glasslike flux lattice is another possibility [Nelson and Seung, 1989]. Others have interpreted this crossover region of the H-T plane as a glass-to-liquid phase transition [Fisher et al., 1989], or the untangling of flux lines [Obukov and Rubinstein, 1990]. I-V characteristics of a Y123 film were interpreted [Koch et al., 1989] using the glass-liquid phase transition model of Fisher et al. [Fisher et al., 1989], but Griessen argued that the Koch et al. data could also be interpreted as due to thermally-assisted flux flow, and that this glass-to-liquid line is equivalent to the depinning line [Griessen, 1990]. The magnetization data of Xu et al. [Xu et al., 1990] on oriented powders of Y123, Bi(2212), and Bi(2223) gave irreversibility temperatures which were not theoretically predicted by either the lattice-melting model or the glass-liquid phase transition model. They suggested instead that the crossover is a depinning line, since the irreversibility temperatures correlated strongly with the pinning strengths of the materials. Despite all of the different experimental techniques and terminologies, it seems that a single physical phenomenon is giving rise to these observations, but the details of this phenomenon are not completely understood [Malozemoff, 1990].

In this dissertation, two of the somewhat "different" high-Tc superconductors were studied, Nd_{1.85}Ce_{0.15}CuO_{4+y} (NCCO) and Ba_{0.8}K_{0.4}BiO_{3} (BKBO). Nd_{1.85}Ce_{0.15}CuO_{4+y} has a transition temperature of 24 K and a tetragonal crystal structure, illustrated in Fig. 1.5a, having CuO_{2} layers similar to the cuprates with higher Tc, but no apical oxygen atoms above the CuO_{2} planes [Tokura et al., 1989; Takagi et al., 1989]. Unlike other high-Tc cuprates, however, NCCO has electron as well as hole carriers [Takagi et al., 1989; Uji et al., 1989]. Initially, it was speculated that only electrons were involved in the superconductivity, since
Fig. 1.5 Crystal structures for different high-\(T_c\) superconductors: (a) \(\text{Nd}_2\text{CuO}_4\), the parent compound for the electron-doped superconductors, (b) \(\text{La}_2\text{CuO}_4\), the parent compound for hole-doped materials, and (c) Ba-K-Bi-O. In (a) and (b), the c-axis is the long axis, and the smaller dark spheres are Cu atoms and the white spheres are oxygen atoms.
the Hall coefficient was found to be negative at all temperatures investigated [Takagi et al., 1989; Uji et al., 1989]. Recently, however, the Hall coefficient has been observed to change sign, and the Seebeck coefficient also has complicated behavior [Lim et al., 1989; Nücker et al., 1989; Wang et al., 1991], both of which indicate that there are both electron and hole carriers involved [Hagen et al., 1991; Xu et al., 1991]. Hidaka and Suzuki [Hidaka and Suzuki, 1989] performed resistivity measurements on a single crystal sample of NCCO and found a nearly parallel shift of the resistivity curve to lower temperatures but no broadening in the resistivity curves with increasing field parallel to the c-axis. This behavior is similar to conventional type-II superconductors, but unlike the hole-doped cuprates. There was broadening, however, when field was applied perpendicular to the c-axis. From the resistivity curves, they obtained $H_{c2}(T)$ curves and zero-temperature coherence lengths $\xi_{ab}=7$ nm and $\xi_c=0.34$ nm, which are lower limit estimates. This gives an anisotropy ratio of about 20, or $\Gamma=400$, which lies between $\text{Y}123$ ($\Gamma=30$) and $\text{Bi}(2212)$ ($\Gamma=3000$). A study of magnetoresistance in thin films of NCCO [Kussmaul et al., 1991] led to the conclusion that NCCO behaves as a stack of almost decoupled two-dimensional metallic sheets, confirming the large anisotropy.

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, with a $T_c$ up to 30 K for $x=0.4$ [Mattheiss et al., 1988; Cava et al., 1988, Battlogg et al., 1988; Hinks et al., 1988], has a cubic perovskite crystal structure [Cava et al., 1988; Pei et al., 1990], shown in Fig. 1.5b, with none of the CuO$_2$ layers which are largely responsible for the superconducting properties of the high-$T_c$ cuprates. In contrast to the cuprates, BKBO is non-magnetic [Cava, 1988], and Hall effect measurements [Kondoh et al., 1989] indicate the charge carriers are electrons. Like the cuprates, however, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is a doped insulator and has a large $T_c/N*(0)$ ratio, where $N*(0)$ is the electronic density of states at the Fermi level [Batlogg et al., 1988]. BKBO appears to be a weak-to-moderate coupling BCS-like superconductor with the high $T_c$ resulting from large
electron-phonon matrix elements involving high-energy phonons [Hinks, 1990; Huang et al., 1990]. The zero-temperature coherence length $\xi(0)$ is approximately 4 nm in BKBO [Kwok et al., 1989; Yang et al., 1990; Savvides et al., 1990], and the GL parameter $\kappa = \lambda / \xi$ is estimated to be 60 [Kwok et al., 1989]. In the resistivity measurements of polycrystalline BKBO, the onset of superconductivity is suppressed with increasing magnetic field, and the transition curves are shifted approximately in parallel to lower temperatures with only a small amount of broadening [Welp et al., 1988; Savvides et al., 1990; Kwok et al., 1989]. This is in contrast to the transition broadening in field observed for the high-$T_c$ cuprates.

This dissertation will describe magnetization measurements on $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (BKBO) and grain-aligned $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{4-y}$ (NCCO) which were carried out in order to study the reversible and irreversible behavior in the field-temperature plane and compare the results with conventional superconductors and other high-$T_c$ superconductors. Chapter 2 will focus on the thermodynamics from which the field-dependence of the specific heat was derived from the reversible magnetization data, and on models used to derive a single effective pinning potential from the flux creep and hysteresis data. Chapter 3 will give the experimental details, including sample preparation and data acquisition. Chapter 4 will present the experimental results and discuss their implications. The conclusions will be presented in Chapter 5.
CHAPTER 2. THEORY AND MODELS

2.1. Reversible Magnetization: Thermodynamics

It was shown by Mapother [1962] that good agreement between calorimetric and magnetically-derived thermodynamic quantities could be obtained for conventional superconductors Sn and In under the condition of thermodynamic reversibility. Good agreement between calorimetric and magnetization-derived specific heat data for YBa$_2$Cu$_3$O$_{7-x}$ has recently been obtained [Gohng and Finnemore, 1990]. The starting point is the Gibbs thermodynamic potential (Gibbs free energy function) $G$, with differential

\[ dG = -SdT + VdP - MdH, \]

where $S$ is the entropy, $V$ is volume, and $P$ is pressure, so that

\[ \left( \frac{\partial G}{\partial T} \right)_{P,H} = -S, \]  

(2.1)

and

\[ \left( \frac{\partial G}{\partial H} \right)_{T,P} = -M. \]  

(2.2)

At constant pressure $P$, the free-energy difference between the fields $H'=0$ and $H=H'$ is

\[ G(H,T) - G(0,T) = -\int_0^{H'} M \, dH' \]  

(2.3)

which corresponds to the area under the magnetization-verses-field (M-vs-H) curve at temperature $T$. Because this is only the change in free-energy with field, $G_H$ or $G_0$ cannot be obtained separately by this method. $G_H$-$G_0$ is sketched in Fig. 2.1a.
Fig. 2.1  (a) Free-energy curves for the normal state, superconducting state with field, and superconducting state without field. (b) Specific heat curves in the superconducting state with and without field; the quantity obtained in this experiment is the difference between these two curves.
For a reversible transformation, an infinitesimal change in the entropy of the system is $dS = dQ/T$, where $dQ$ is an infinitesimal amount of heat transferred, and the definition of specific heat is $C_p = (dQ/dT)_p$. It follows that

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p.$$ \hspace{1cm} (2.4)

Combining (2.4) with (2.1) and (2.3) gives

$$C_o - C_H = T\left[\frac{d^2(G_H - G_o)}{dT^2}\right]$$ \hspace{1cm} (2.5)

which is the difference in specific heat of the superconductor with and without an applied field. This is sketched in Fig. 2.1b.

2.2. Irreversible Magnetization

2.2.1. Critical State Model

In the irreversible region of the H-T plane, Abrikosov vortices can be pinned (resist electromagnetic driving forces) by microstructural defects such as grain boundaries, voids, precipitates, inclusions, twin planes, strain fields, and stacking faults [Campbell and Evetts, 1972]. At $T=0$, the vortices in the bulk of the superconductor can move only if the driving force density exceeds the local pinning-force density [Tinkham, 1975]. In the critical state, the fluxoids are distributed such that the driving force density equals the pinning force density throughout the sample [Bean, 1962, 1964; Kim et al., 1963].
It is energetically favorable for the vortices to be pinned in defect locations as opposed to regions of bulk superconductivity because the mean free path $l$ of the electrons in the region of the defect is decreased, and, since the dirty-limit coherence distance $\xi$ is related to the mean free path by $\xi(T) = 0.855(\xi_0/l)^{1/2} / (1 - T/T_c)^{1/2}$, and the free energy per unit length of a vortex is related to $\xi$ by $\Delta F / L = (H_c^2 / 8\pi)\xi^2$. The free energy difference per unit length by pinning on the defect is then proportional to $l_D - l_B$, where $l_D$ is the mean free path at the defect and $l_B$ is the bulk mean free path. Since this difference is negative, the defect is the preferred location for the vortex.

In the absence of flux pinning, i.e. for a perfectly-homogeneous superconductor, the application of an external field $H_a > H_{c1}$ would result in a uniform flux density within the interior of the sample. This is depicted for a magnetic field parallel to the axis of a long cylindrical sample with radius $R$ in Fig. 2.2a. Here there is no bulk screening current, only the Meissner screening current which exists approximately one penetration distance $\lambda$ from the cylinder's surface and persists until $H_a$ approaches $H_{c2}$, at which time diamagnetism disappears. If pinning is present, however, then the flux density in the sample varies as a function of position, and macroscopic screening currents, in addition to the Meissner currents, are induced within the sample.

The Bean model [Bean, 1962, 1964] assumes that the flux density gradient caused by pinning is constant within the sample, and independent of the applied field value. This is sketched for two field values in Fig. 2.2b for the sample geometry discussed above. In both cases, the applied field is larger than $H^*$, the field at which the flux front first penetrates to the center of the sample. The critical current density $J_c$ is proportional to the slope of the flux profile, so in this case $J_c$ is constant, since it is related to the flux density profile by Ampere's Law $\partial H / \partial r = (4\pi / c)J_c$. In high fields $H >> H_a$, $\partial B / \partial H \sim 1$, so...
Fig. 2.2 Flux density profiles in a cylindrical sample of radius R under different conditions assuming the Bean model: (a) ideal superconductor with no pinning; (b) superconductor with pinning; (c) field-increasing case (B+) and field-decreasing case (B−)
In an M-vs-H measurement, a sample with pinning will exhibit hysteresis, so that at the same value of applied field, \( M \) will depend on whether the field was previously increasing \((H_a^+)\) or decreasing \((H_a^-)\). The local magnetic flux density is illustrated for the field-increasing and field-decreasing cases in Fig. 2.2c. At the specimen surface, \( B_s = H_a + 4\pi M_{eq} = B_{eq}(H_a) \), since the parallel component of \( H \) is continuous [Jackson, 1975], and for \( r > R \), \( B = B_{eq}(H_a) \), where \( B_{eq}(H_a) \) is the value that \( B \) would have in the absence of pinning (the equilibrium value). The local flux density \( B(r) \) is

\[
B_{\pm}(r) = B_s \mp \frac{4\pi}{c} J_c(R-r)
\]

The magnetization is related to the average flux density by \( \langle B \rangle = 4\pi M + H_a \), and the magnetization hysteresis is \( \Delta(-4\pi M) = -4\pi M(H_a^+) - (-4\pi M(H_a^-)) \). Therefore, the local flux density must be integrated to obtain the hysteresis \( \Delta(-4\pi M) = \langle B_+ \rangle - \langle B_- \rangle \).

\[
\langle B_+ \rangle - \langle B_- \rangle = \frac{1}{\pi r^2} \int_0^{2\pi} d\phi \int_0^r \frac{8\pi}{c} J_c(R-r) r \, dr
\]

\[
= \frac{8\pi}{3c} J_c R
\]

In practical units of gauss, A/cm^2, and cm, the result is

\[
\Delta(-4\pi M) = \frac{4\pi}{15} J_c R
\]

(2.6)

If the sample is a sphere rather than a cylinder, the 15 is replaced by 17.

The Bean model assumes a field-independent \( J_c \). Several other models exist which are more sophisticated and account for the field dependence of \( J_c \) under certain
circumstances. For example the Kim model [Kim et al., 1962] gives \( J_c(H,T) = J_c(T)/(1+H/H_0) \), the power-law model [Irie and Yamafuji, 1967] gives \( J_c(H,T) = K(T)/H^n \), and the exponential model [Fietz et al., 1964] gives \( J_c(H,T) = J_c(T)\exp(-H/H_0) \). A generalized critical state model proposed by M. Xu et al. [M. Xu et al., 1990] reduces to the above expressions in the appropriate limits. These models are used mostly for low field data. In this thesis work, the data were generally taken at high fields \( H >> H^* \), and so \( B \sim H \), giving a nearly uniform \( J_c \) across the sample. The Bean model was therefore a reasonable approximation.

2.2.2. Anderson-Kim Flux Creep

Thermally-activated motion of Abrikosov vortices past pinning centers was addressed in the Anderson-Kim flux creep model [Anderson, 1962; Anderson and Kim, 1964] in order to account for the large low-temperature temperature-dependence of the pinning force in Nb-Zr tubes [Kim et al., 1962]. They assumed that a group of several vortices, a flux bundle, as opposed to a single vortex, moves independently out of a pinning site by thermal activation. This is justified by the fact that the vortices interact via a repulsive force over a distance on the order of the penetration depth \( \lambda \), which is roughly the spatial extent of the magnetic field of a vortex. It is very energetically unfavorable to have local perturbations in the vortex density; therefore a single vortex jumping over a pinning barrier would become out of equilibrium with the surrounding flux density. It is not a single vortex that moves over a pinning barrier, but a bundle of vortices with a radius on the order of \( \lambda \) [Anderson, 1962]. Since \( \lambda \) for a conventional hard superconductor is typically 10-100 nm (and is larger for high-Tc materials), and the intervortex spacing \( a = (\Phi/\lambda)^{1/2} \) is on the order of 10 nm, a flux bundle may typically contain about 100 vortices.
In the extreme case of a defect completely pinning the entire flux bundle (the defect region being entirely non-superconducting), the height of the barrier (free energy of the barrier) with no external driving forces is given by

$$\Delta F_{\text{max}} \equiv (F_n - F_s)d^3 = \frac{H_c^2}{8\pi}d^3,$$

where $H_c$ is the bulk thermodynamic critical field, and $d^3$ is the volume of the flux bundle.

To accommodate the more likely case of less than total pinning of the entire bundle, Anderson also inserted a fraction $p$ to account for the effective volume pinned, leading to

$$\Delta F = p\Delta F_{\text{max}} = p\frac{H_c^2}{8\pi}d^3.$$

In the presence of a current (due to a non-uniform flux density in the critical state), there will be a Lorentz force (per unit volume) $J_c \times \mathbf{B}/c$. This is integrated over the volume of the flux bundle and multiplied by the hopping distance to obtain the free energy contribution due to the Lorentz force

$$F_L = -J_cBd^4 = -J_c\Phi d^2,$$

where $\Phi$ is the total flux in the bundle. The free energy that the bundle must acquire to hop out of the pinning well is then

$$\Delta F = \frac{H_c^2}{8\pi}d^3 - J_c\Phi d^2.$$

(2.7)

This free energy both with and without a driving force is depicted schematically for a hypothetical distribution of pinning sites in Fig. 2.3. Here, $U_0$ signifies the pinning potential in the absence of a driving force. A driving force such as the presence of the critical current effectively tilts the potential (the so-called "tilted washboard"), which decreases the height
Fig. 2.3  Pinning barrier in Anderson-Kim flux creep model: (a) without driving force; (b) with driving force
of the barrier seen by the bundle and makes the bundle more susceptible to thermal activation out of the well in the direction of decreasing flux density. This approximation to the pinning potential is the linear approximation because it is assumed that $U \propto J$.

Anderson showed that the hopping rate of the bundle due to thermal activation is $R = R_0 e^{-\Delta E/kT}$, where $R_0$ is an attempt frequency. Starting from this rate equation, the critical state parameter $\alpha(t) = J(t) [B(t) + B_0]$ was shown to decay logarithmically in time. This model of Anderson gives some physical insight to the process of thermally-activated flux motion, and it was the starting point for the flux creep model of Beasley et al. [Beasley et al., 1969].

### 2.2.3 Beasley Model

The Beasley model [Beasley et al., 1969] is based on Anderson model [Anderson, 1962] of thermal activation discussed above. To formulate the equations necessary to relate material-sensitive parameters to characteristic quantities describing the flux creep process, Beasley et al. extended Anderson results. The starting point of the Beasley model is a diffusion equation for flux transport which originates from the condition of conservation of flux

$$ \frac{\partial B}{\partial t} = -\nabla \cdot \mathbf{D}, $$

where

$$ \mathbf{D} = -(\nabla B / |\nabla B|) B w v_0 e^{-U_B(|\nabla B|)/kT} $$

is the flux flow density. This flux flow density $\mathbf{D}$ is the amount of flux crossing a line perpendicular to $B$ and $\nabla B$ per unit length and time; $w$ is the average distance moved by a
flux bundle during a thermally-activated jump, and $\nu_0$ is the attempt frequency. This leads to the flux creep equation

$$\frac{dB}{dt} = \nabla \cdot \left( \frac{(\nabla B/|\nabla B|) B}{V} \right) \nu_0 e^{-U/RT}$$

(2.8)

Once the solution for $D$ is found, the total flux $\Phi$ in the sample, an experimentally observable quantity, can be obtained from the relation

$$\frac{d\Phi}{dt} = -2\pi pD(p,t)$$

where $p$ is the sample radius. Beasley et al. solved Eq. 2.8 for the geometry of a solid cylinder using the simplifying assumptions of no significant surface barrier effects, and $U = (U_0 - FVX) \gg kT$, which is expected to hold in the critical state. The result for the creep rate $R = d\Phi/d\ln t$ is

$$R = \pm \frac{1}{3} \pi kT \rho \left( \frac{\partial U}{\partial |\nabla B|} \right)^{-1} (1 \pm \delta),$$

where

$$\delta = \pm \frac{1}{3} |\nabla B| \frac{\partial}{\partial B} \ln \left[ \frac{1}{|\nabla B|} \left( \frac{\partial U}{\partial |\nabla B|} \right) \right].$$

is a small correction factor. In the case of large driving forces so that $U \ll U_0$ and the thermal activation takes place near the top of the energy barrier, the parameter $U_0$ is not trivially related to the true barrier height $U_p$. This is illustrated in Fig. 2.4; the slope of the $U$-vs-$\nabla H$ curve is

$$\left( \frac{\partial U}{\partial |\nabla B|} \right) = \frac{U_0}{4\pi J_c/c}$$

(2.9)
Fig. 2.4 Figure from Beasley et al. showing the dependence of $U$ on $J_c$. Using the linear approximation gives $U_0$ as the intercept of the tangent to the curve at the point shown.
in the limit $U \ll U_0$, which is known as the linear approximation. The creep rate equation can now be written as

$$R = \frac{\pi}{3} kT \rho \left( \frac{4\pi J_c}{c} \frac{1}{U_0} \right) (1 \pm \delta).$$

(2.10)

where

$$\delta = \frac{1}{2} \left( \frac{4\pi}{c} \right) \rho \left( \frac{1}{2} J_c \frac{\partial \ln U_0}{\partial B} - \frac{\partial J_c}{\partial B} \right).$$

In most cases, delta (which is usually small compared to unity) is eliminated by using $R_{\text{avg}} = (R_+ + R_-)/2$, where $R_+$ and $R_-$ are the field-increasing and field-decreasing creep rates respectively, and

$$\frac{R_+}{R_-} = \frac{(1 + \delta)}{(1 - \delta)}.$$

In the present study, the observable quantity was the magnetization. Using $\Phi = BA = B\pi\rho^2$, $4\pi M = B - H$, and $S = dM/d\text{Int}$ gives

$$\frac{U_0}{kT} = \frac{\rho J_c}{30S}.$$ 

(2.11)

By measuring the flux creep rate $S$ and critical current density $J_c$, it is possible to derive an effective pinning potential $U_0$, which is a material-sensitive parameter. One must keep in mind, however, that the observable quantity $U_0$ is not the actual barrier height, but is related to it.
CHAPTER 3. EXPERIMENTAL PROCEDURES

3.1. Sample Preparation

3.1.1. Nd<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>y</sub>

Because of the large anisotropies in the high-\(T_c\) superconductors, randomly-oriented polycrystalline samples are often not suitable for measuring intrinsic physical properties. The physical properties along the c-axis differ from those in the a-b plane by large factors, so grain orientation is required for meaningful measurements. Because the anisotropy within the a-b plane is small, the most important alignment is to orient the c-axis of the grains. The three most common types of oriented samples are single crystals, epitaxial thin films, and grain-aligned polycrystalline samples. In epitaxial thin films, the c-axis often is perpendicular to the film surface, but the a and b axis are only partially oriented. For grain-aligned samples the c-axis of all grains is within a few degrees, the a and b axes are random. In most cases, proper oxygen stoichiometry is crucial for obtaining reproducible physical properties. Grain-aligned samples [Farrell et al., 1987] have the advantage that each single-crystal grain is quite small (approximately 20 \(\mu\)m in diameter), which facilitates complete oxygen diffusion. The main disadvantage is the small degree of misalignment, especially when measuring with the applied field perpendicular to the c-axis.

The Nd<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>y</sub> (NCCO) sample consisted of grains crystallographically-aligned in epoxy [Hyun et al., 1989]. The first step was the preparation of polycrystalline NCCO using solid state reaction [Tokura et al., 1989]. Powders of Nd<sub>2</sub>O<sub>3</sub> (Ames Lab 99.999% pure), Ce<sub>2</sub>O<sub>3</sub>, (Ames Lab 99.99%), and CuO (Fisher 99.999%) were ground and sintered in air at 950 \(^\circ\)C for 16 h. This sintering was repeated twice with intermediate
grinding. The material was then reground, pressed into pellets, and sintered in air for 20 h at 1150°C before air quenching. At this point, the sample was not superconducting. Superconductivity was obtained by annealing the sample in flowing N₂ at 915°C for 1 day before furnace cooling. The magnetization data of Fig. 3.1a taken at a field of 100 Oe show an initial decrease in the magnetization value at T=24 K.

To achieve grain alignment, the pellets were ground to a grain size of about 20 μm, mixed with outgassed epoxy (EPOTEK 301), and poured into a Teflon container. This container was rotated about an axis perpendicular to a 2.4 T magnetic field. Because the magnetic susceptibility of NCCO at room temperature is largest in the crystallographic a-b plane, the c-axis of the individual grains gradually align along the rotation axis. EPOTEK 301 epoxy is a low-viscosity material with a small magnetic susceptibility (-6.6x10⁻⁷ emu/g) over the field and temperature range of interest. The viscosity increases relatively little over the first hour after mixing, and good alignment was achieved by rotating the powder/epoxy mixture for 6, 3, and 1 rpm for 1 h each, followed by 0.5 rpm for more than 6 h in the 2.4 T field.

The quality of the grain alignment was evaluated using x-ray diffraction. Two flat-plate samples, one with the c-axis parallel to the flat surface and one with the c-axis perpendicular to the flat surface were prepared for this purpose. Figure 3.2 shows the x-ray powder diffraction patterns for these samples and for a randomly-oriented powder sample. With the c-axis perpendicular to the surface, the (00l) lines of inset b are greatly enhanced compared to the random powder sample of inset a, while the other lines are suppressed into the noise. With the c-axis parallel to the surface, the (hk0) lines are enhanced, as shown in Fig. 3.2(c). The rocking curve for the (006) peak in Fig. 3.2(d) reflects the mosaic spread of the grains and is a quantitative measure of the grain alignment. The full-width-at-half-maximum (FWHM) value of about 3 degrees is larger than the 1.8 degrees typically obtained
Fig. 3.1  
Low-field magnetization curves for (a) NCCO and (b) BKBO
Fig. 3.2  X-ray diffraction study of the grain alignment in NCCO: (a) random powder; (b) c-axis perpendicular to surface; (c) c-axis parallel to surface; (d) rocking curve for the (006) peak
for YBa$_2$Cu$_3$O$_{7.6}$ (Y123) [Farrell et al., 1987]. This is because the NCCO particles do not
fracture along grain boundaries as consistently as the Y123, and therefore some of the
particles are bicrystals, as illustrated by the optical micrograph of Fig. 3.3.

Four different cylindrical grain-aligned samples, with diameters of 3 mm and lengths
of approximately 3 mm, were measured in the magnetometer. Two of the samples were
superconducting; one with the c-axis parallel to the cylinder axis and one perpendicular to
the cylinder axis. The other two were non-superconducting samples with the same
orientations as the superconductors. These non-superconductors, used for normal-state
background subtraction as discussed below, were made by reoxygenating powder from the
original superconducting batch at 925 C for 20 h in flowing oxygen gas, cooling to 700 C
over 5 h, and furnace-cooling to room temperature. The grain alignment was carried out in
the same way as for the superconducting samples. For the magnetization measurements,
each sample was mounted in a quartz tube necked-down in the center to prevent the sample
from slipping.

3.1.2. Ba$_{0.6}$K$_{0.4}$BiO$_3$

The Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO) sample consisted of powder in EPOTEK 301 epoxy.
Grain alignment was not attempted since this material has a cubic crystal structure. The
powder was cured in epoxy solely to achieve a similarity to the NCCO sample, i.e.,
electrically-isolated grains.

Polycrystalline BKBO was prepared [Hinks et al., 1988] by grinding stoichiometric
amounts of BaO (>98% purity), KO$_2$ (>90% pure - Aldrich), and Bi$_2$O$_3$ (99.9% pure -
Fisher), annealing at 750 C in flowing N$_2$ for 1 h, and regrinding in an N$_2$ environment. At
this point, the powder was reddish-brown and non-superconducting. The powder was then
Fig 3.3 Optical micrographs of grain-aligned NCCO. The direction normal to the page is (a) perpendicular to the c-axis, and (b) parallel to the c-axis.
oxygenated at 550°C in flowing O₂ for 1 h which yielded a dark blue-black superconducting powder.

The powder x-ray diffraction pattern in Fig. 3.4 confirms that no impurity phases exceeding about 5% are present. The most intense lines in the pattern belong to the silicon reference standard. An optical micrograph of the powder/epoxy composite is shown in Fig. 3.5. The sample was mounted in a quartz tube as described for NCCO. The initial decrease in magnetization occurs at T=27 K in a field of 10 Oe as shown in Fig. 3.1b.

3.2. Magnetization Measurements

Magnetization measurements were conducted in two commercial Quantum Design superconducting quantum interference device (SQUID) magnetometers, an older one (the prototype instrument) with maximum magnetic field capability of 2 T ("QD1"), and a newer one (serial number 138) with 5.5 T capability ("QD2"). The NCCO samples were measured primarily in QD1 using a scan length of 3.5 cm, over which the magnetic field was homogeneous to 0.2%. In this case, the software employed the peak-to-peak method to calculate the magnetic moment from the voltage-verses-position profile as the sample was pulled through the second-derivative gradiometer pickup coils. BKBO was measured in QD2 using a 3.0 cm scan and iterative regression analysis to calculate the magnetic moment. The field was uniform to 0.05% over this distance.

Three basic types of measurements were made: (1) magnetization-verses-temperature (M-vs-T), (2) magnetization-verses-field (M-vs-H), and (3) magnetization-verses-time (M-vs-t). M-vs-T measurements consisted of either zero-field-cooled (ZFC) or field-cooled (while) warming (FCW; alternately field-cooled rewarming FCR) sequences. In ZFC sequences, the sample was cooled in zero field (a small remnant field, about 1-20 Oe,
Fig. 3.4  X-ray diffraction pattern for BKBO. The peaks of highest intensity are for the silicon reference standard.
Fig. 3.5  Optical micrograph of a BKBO powder/epoxy composite made with the original batch of powder. The grains are the lighter colored particles, and voids are present in the epoxy due to lack of outgassing prior to mixing. The sample on which the measurements were made was outgassed before mixing.
was always present) from a temperature above T_c to the initial measuring temperature. (In QD2, degaussing to minimize the residual field was done by setting 4T, -4T, 0T in the oscillating-field mode. In QD1 a damped-oscillating sequence starting at -500 Oe and oscillating about zero was used.) Field was applied, and measurements were taken as the temperature was increased, typically in increments of 1.0 K. Then the temperature was lowered from above T_c to the initial measuring temperature without changing the field, and the measurements (FCW) were repeated during warming. "Field-Cooled-Warming" (FCW) is used [Clem, 1991b] instead of "field-cooled" (FC) since this terminology more precisely describes the measurement, and in the irreversible region of the H-T plane the precise nature of the field and temperature history has a significant impact on the measurement results. M-vs-H measurements were generally in the form of hysteresis loops, where the sample was cooled in zero field to the measuring temperature, and a large negative field (-2 T for QD1, -5 T for QD2) was applied (in direct, non-oscillating mode) and removed. Measurements were then taken as the field was incrementally increased in direct mode up to a maximum value and decreased to zero. Several measurements were taken at each field setting to monitor the magnetic relaxation over time. Time-dependent magnetization was also studied using ZFC M-vs-t measurements, in which the sample was cooled from above T_c to the measuring temperature in zero field, a field applied, and magnetization recorded over time.

Demagnetization effects were not corrected for in either the NCCO or BKBO. In both cases the grain shapes were roughly isotropic, so taking a demagnetization factor of 1/3 (the value for a sphere) and using the equation \( H_{\text{internal}} = H_{\text{applied}} - (1/3)4\pi M \) resulted in a 4% correction at 6 K and 0.1 T (H \( \parallel c \), ZFC) for NCCO, and a 9% correction at 5 K and 0.1 T for BKBO. These corrections become smaller at higher temperatures and fields. For example, at 1 T and 6 K for NCCO the correction is only 0.08 %, and at 1 T and 5 K for
BKBO the correction is only 0.2%. The error in $G(H) - G(0)$ caused by ignoring the demagnetization factor is negligible once the field is high enough.
CHAPTER 4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Magnetization of Nd_{1.85}Ce_{0.15}CuO_{4-y}

4.1.1. Irreversibility Crossover

In the reversible region of the H-T plane, magnetic flux moves reversibly into and out of the sample as the field is applied and removed. In the irreversible region, magnetic flux is pinned, but, over time, flux creep can occur, and the magnetization relaxes. To determine the boundary between these two regions, a crossover line $H_{irr}(T)$ or $T_{irr}(H)$ (commonly referred to as the "irreversibility line") was obtained by plotting the difference in the ZFC and FCW moment-vs-T curves and defining $T_{irr}(H)$ to be the temperature where the difference became smaller than $10^{-4}$ emu, near the limit of the measurement.

The familiar positive curvature of $H_{irr}(T)$ in the H-T plane observed in the other high-$T_c$ superconductors is observed in NCCO, as shown in Fig. 4.1. The log-log plot of $(1-T/T_c)$-vs-$H_{irr}$ in Fig. 4.2 has a slope of about 0.3 for both $H \parallel c$ and $H \perp c$, rather than the value of 0.67 commonly found for Y123, [Yeshurun and Malozemoff, 1988; Y. Xu et al., 1990] and predicted [Yeshurun and Malozemoff, 1988] by a scaling argument based on the Anderson-Kim flux creep model and using the temperature dependences of the superconducting coherence length $\xi(T)$ and the thermodynamic critical field $H_c(T)$ from the clean-limit Ginzburg-Landau theory. A similar value of approximately 0.3 was observed in a Bi$_2$Sr$_2$CaCu$_2$O$_{8+}$ single-crystal for both field orientations [Kritscha et al., 1991]. In grain-aligned (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ with $H \parallel c$, a slope of about 0.3 was also found [Green et al., 1991] if the irreversibility points were extrapolated using fitted curves as described in Ref.
Irreversibility crossover using the 0.1 memu criterion for field parallel (solid squares) and perpendicular (solid triangles) to the c-axis in NCCO
Fig. 4.2 Log-log plots of $(1-T/T_c)$-vs-$H_{irr}$ for NCCO with (a) $H \parallel c$ and (b) $H \perp c$
No phenomenological model exists at this time to explain the value of 0.3.

For $H \perp c$, $H_{\text{int}}(T)$ is shifted to higher temperatures and fields. This NCCO sample exhibits larger hysteresis and larger pinning energies for $H \perp c$, at least at higher fields, which will be discussed in more detail below. The connection between enhanced pinning and shifted irreversibility lines is supported by experiments on 580-MeV Sn-ion-irradiated Y123 crystals, [Civale et al., 1991] which exhibited larger hysteresis and a shifted irreversibility line after irradiation, and a neutron-irradiated Bi 2212 crystal, [Kritscha et al., 1990] which showed similar behavior.

4.1.2. Background Subtraction for NCCO

The total magnetization of NCCO has a paramagnetic contribution from the Nd and Ce ions which dominates the superconducting contribution at large fields and low temperatures. For example, at 1 T and 14 K the superconducting magnetization is only 8% of the total magnetization for $H \parallel c$. Two different background subtraction methods were tried. In the first method, the data points above $T_c$ were fit with the function $\chi = \chi_0 + C/(T - \Theta)$, which was then extrapolated below $T_c$ and subtracted from the total magnetization under the assumption that the superconducting contribution does not change the normal state background below $T_c$. In the second method the non-superconducting sample was measured at each temperature and field, and the values subtracted from the total magnetization of the superconducting sample. Above 25 K, the non-superconducting and superconducting samples had the same magnetization to within 3% (a small linear term probably arising from the mass uncertainty was also subtracted), and we assumed that below $T_c$ the same normal-state crystal field levels existed for both cases. In other words, we assumed that changing the carrier concentration by adding oxygen doesn't change the Nd moment. The two
background-subtraction methods gave essentially the same results for the field dependence of the specific heat jump near $T_c$; for example, the peak value of $C_0-C_{0.5T}$ was only changed by 2% and the peak value of $C_0-C_{1T}$ was changed by 10%. An example of the background subtraction is shown in Fig. 4.3.

4.1.3. Reversible Magnetization of NCCO

The upper critical field $H_{c2}$ for the high-$T_c$ superconductors must be discussed with some care. In conventional low-$T_c$ superconductors, the onset of mean-field diamagnetism and the onset of critical currents occur at virtually the same line in the H-T plane. In the high-$T_c$ materials, however, there is a region where the magnetization is thermodynamically reversible separating the onset of diamagnetism and the onset of critical currents [Malozemoff, 1989; 1990]. Furthermore, the mean-field onset of superconducting diamagnetism ($H_{c2}$) is obscured by diamagnetic fluctuations in this region. It is now recognized [Hao et al., 1991] that because of the dominance of diamagnetic fluctuations near $T_c$, the approach of using the Abrikosov high-field result [Abrikosov, 1957] to determine $H_{c2}$ for these materials is not useful. Abrikosov's theory, based on the Ginzburg-Landau equations [Ginzburg and Landau, 1950], predicts a linear region in M-vs-T just below $T_c$, and attempts were made to fit the linear portion of the M-vs-T curve and extrapolate to M=0 to obtain $T_{c2}$ [Welp et al., 1989]. Two problems arise from this approach. First, Abrikosov's theory predicts a field-independent slope $dM/dT$, contrary to what is observed experimentally. Second, the M-vs-T region where the Ginzburg-Landau theory is strictly applicable (very near $T_c$) is not linear, but rounded because of the fluctuation effects. The London model [deGennes, 1966; Fetter, 1969; Kogan et al., 1988] may also be inadequate [Hao and Clem, 1991a], because it neglects the free energy of the vortex cores. Hao et al. [Hao et al., 1991] have developed a model which accounts for the contribution of the vortex
Fig. 4.3  (a) Background susceptibility subtraction for NCCO for $\mu_0 H=0.5T$ with $H \parallel c$.
(b) Enlargement of (a) to illustrate the additional subtraction of a linear offset.
cores to the free energy and is able to describe the experimental magnetization curves in detail. From this model, which is applicable at temperatures between the irreversibility line and fluctuation onset, \( H_{c2} \) can be derived unambiguously. For the case of Y123 [Hao et al., 1991], the correction caused by using model of Hao et al. rather than the Abrikosov high-field result is about 20%.

In this work, \( H_{c2}(T) \) for both field orientations has been estimated using the same approach used by Welp et al. for Y123, that is, extrapolating the linear portion of the M-vs-T curve to M=0 and calling the intersection \( T_{c2} \). As discussed above, this approach is not strictly valid, and an error of 20% or more for \( dH_{c2}/dT \) should be expected. Figure 4.4 shows the M-vs-T curves and the extrapolation of the line at \( \mu_0 H = 0.1 \) T. \( H_{c2}(T) \) curves for NCCO are illustrated along with \( H_{in}(T) \) in Fig. 4.5. \( H_{c2}(T) \) rises more rapidly for \( H \perp c \), with slope \( dH_{c2}/dT = -4 \) T/K, than for \( H \parallel c \), which has slope \( dH_{c2}/dT = -1 \) T/K.

In the reversible region of the H-T plane, the equilibrium magnetization is established as fast as the measurement can be made, about one minute, so the change in free energy with changing field, \( G_H - G_0 \), is well-defined. The temperature range is extended a small amount at the lowest fields (from 15.8 K to 14 K at 0.05 T, for example) by assuming the Bean model [Bean, 1962, 1964] is valid here and using the average of the ZFC and FCW magnetization. \( G_H - G_0 \) is derived from the M-vs-T data in the following way. First, the M-vs-T data for each field are transcribed to M-vs-H curves at constant T. Each M-vs-H curve is fit with a fourth-degree polynomial which is then integrated to obtain \( G_H - G_0 \) from Eqn. 2.3. Curves of M-vs-T and M-vs-H, and \( (G_H - G_0) \)-vs-T for \( H \parallel c \) and \( H \perp c \) are presented in Fig. 4.6 and Fig. 4.7 respectively. Free-energy curves for NCCO are qualitatively similar to the curves obtained for Tl(2212) and Tl(2223) [Fang et al., 1989], and Y123 [Athreya et al., 1988; Gohng and Finnemore, 1990] in that they exhibit curvature near \( T_c \), but almost no curvature several degrees below \( T_c \) (about 17K in this case).
Fig. 4.4 Determination of $H_{c2}(T)$ by the linear extrapolation of the reversible magnetization to the $M=0$ line in NCCO
Fig. 4.5 Upper critical field $H_c(T)$ lines obtained from the linear extrapolation method along with the irreversibility crossover in NCCO for both $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \perp \mathbf{c}$. The slopes $dH_c/dT$ were determined to be $-4 \ T/K$ and $-1 \ T/K$ for $\mathbf{H} \perp \mathbf{c}$ and $\mathbf{H} \parallel \mathbf{c}$ respectively.
Fig. 4.6  Background-subtracted curves of (a) $4\pi M$-vs-$T$ and (b) $4\pi M$-vs-$H$ for NCCO with $H \parallel c$.
Fig. 4.7 G(H)-G(0) curves for NCCO with (a) $H \parallel c$ and (b) $H \perp c$
The field dependence of the specific heat jump, \( C_0 - C_H \), is related to the curvature in \( G_H - G_0 \) by Eqn. 2.5. The second derivative is obtained by fitting the first 5 points of the \((G_H - G_0)\)-vs-T curve with a third-degree polynomial which is differentiated twice and evaluated at the center (third) temperature. Then the next temperature is added, the first temperature discarded, and the process repeated until the end of the \((G_H - G_0)\)-vs-T curve is reached. Other differentiation methods were tried and gave the same results within 10%.

The behavior of \( C_0 - C_H \), presented in Fig. 4.8, is qualitatively similar to other high-\( T_c \) cuprates. The onset of the broad fluctuation peak near \( T_c \) is shifted relatively little in temperature as the field is increased to 2 T, and at lower temperatures the specific heat is nearly independent of field. The main effect of the applied field is to broaden and suppress the amplitude of the specific heat jump without suppressing the onset temperature of the jump [Sanders et al., 1990]. This behavior was observed in the other cuprate superconductors in direct calorimetric measurements of Y123 [Salamon et al., 1988; Salamon et al., 1990; Inderhees et al., 1991; Bonjour et al. 1990] and multiphase Bi and Tl HTSC compounds [Fisher et al., 1988], and in magnetic measurements of Y123 [Athreya et al., 1988; Gohng and Finnemore, 1990] and Tl2223 [Fang et al., 1989] This is in complete contrast to conventional type-II superconductors [Cors et al., 1990], in which the temperature where the \( C_p \) jump occurs is steadily suppressed along the \( H_{c2}(T) \) line with relatively little shape change as magnetic field is increased. The field-dependence of the specific heat jump in Y123 has been fit [Inderhees et al., 1991] by taking into account critical fluctuation effects; it may be that these effects are playing a role in NCCO as well. The results of Fig. 4.8 give only the change in specific heat with field, not the total jump in \( C_p \). It is clear, however, that there must be a specific heat jump \( \Delta C_p \) greater than \( C_0 - C_{H=0} \) which is about 1.2 mJ/cm\(^3\)K or 0.16 mJ/gK. This is to be compared with 4 mJ/cm\(^3\)K for Tl(2223), 3 mJ/cm\(^3\)K for Tl(2212) [Fang et al., 1989], and 21 mJ/cm\(^3\)K for Y123 [Gohng and Finnemore, 1990]. An anisotropy
Fig. 4.8 Field-dependence of the specific heat near $T_c$ for NCCO with (a) $\mathbf{H} \parallel \mathbf{c}$ and (b) $\mathbf{H} \perp \mathbf{c}$
of about 2.5 between the peak values for $H \parallel c$ and $H \perp c$ was observed for NCCO, compared to 5 for Y123 [Athreya et al., 1988].

4.1.4. Irreversible Magnetization of NCCO

The melting of the flux line lattice is more like the melting of a glass than it is like the melting of ice, in that the lattice gradually softens as temperature is increased. The irreversibility line in high-$T_c$ superconductors is difficult to measure because the idea of thermodynamic reversibility implies the long-time equilibrium limit. In any measurement the time scale is finite, and the transition from reversible to irreversible behavior occurs gradually. Here, $H_{irr}(T)$ is viewed a crossover region, and, starting from flux creep and hysteresis data, we parameterize the data in terms of an effective pinning potential.

Flux pinning and flux creep for both $H \parallel c$ and $H \perp c$ were measured in order to study the transformation from the reversible to the irreversible regime in NCCO. The goal was to use simplified models, the Bean model for critical currents and the Beasley model for flux pinning energies (both described in Chapter 2), to qualitatively study pinning and compare trends in pinning behavior between the two orientations of NCCO, as well other superconductors. It must be emphasized that the purpose of this study was not to obtain quantitative values for pinning energies, but only to help identify broad, relative trends among the different samples. By parameterizing the data in terms of an effective pinning potential, it is possible to determine which areas of the H-T plane are in the crossover from a rigid pinned flux line lattice to the reversible range. At present there is no theory that enables one to parameterize these data in terms of the details of the pinning.

The region of applicability of the Beasley model [Beasley et al., 1969] was addressed by Lichtenberger et al. [Lichtenberger et al., 1991]. The two requirements are that the creep is logarithmic in time and that analysis is restricted to fields larger than the full penetration
field $H^*$. $H^*$ was not systematically determined for this sample, but it was smaller than about 0.05 T over the temperatures of interest here. Low field creep rate-vs-field data at $T=4$ K are displayed in Fig. 4.9. The peak in the creep rate occurs at about 0.05 T, and $H^*$ is expected to lie slightly below this peak [Lichtenberger, 1991]. Furthermore, $H^*$ is expected to decrease as temperature increases [M. Xu et al., 1991]. Therefore, all of the analysis for NCCO takes place at sufficiently high fields. The magnetic relaxation of Fig. 4.10 was closely logarithmic in time, with only a slight rounding detectable. Experience has shown that the initial points are rather sensitive to error in the initial measurement time $t_0$, which may account for deviation at small times. No creep data were taken at temperatures higher than 10K. The Beasley model [Beasley et al., 1969] is a simplified model in that it assumes a single effective pinning potential when there is very likely a distribution of pinning energies [Hagen and Griessen, 1989]. The one-potential model has the advantage in that a single effective pinning energy can be obtained and at each point in the $H$-$T$ plane. This makes it more convenient to compare pinning in different materials.

Three methods were used to measure flux creep in NCCO. Only one method need be used, but three methods were tried in order to determine the difference in the final result, the effective pinning potential, caused by the details of the measurement method. In the first method, the relaxation toward equilibrium was studied at each field of the isothermal $M$-vs-$H$ hysteresis loops. Five data points acquired over about 7 minutes were taken at each field step for increasing and decreasing field. Flux creep rates were determined by fitting the last 4 (out of 5) points of the $4\pi M$-vs-$(\ln t)$ data to a straight line to get a slope $4\pi S$, where $S=dM/d(\ln t)$. In the second method, the sample was cooled from above $T_c$ to the measurement temperature in zero field (ZFC), the field was applied in direct, non-oscillating mode, and the magnetization measured 10 times over a period of about 15 minutes. In this case the creep rate was obtained by fitting a straight line to the final 4 (out of 10) points of
Fig. 4.9  Low-field creep rate data at $T=4$ K for NCCO with $H \parallel c$. The full-penetration field $H^*$ for this sample is approximately 0.05 T
Fig. 4.10  Comparison of magnetic relaxation using different methods in NCCO at $T=6$ K and $\mu_0H= (a) 0.1$ T and (b) 0.2 T. The three different methods are described in the text. Note that the horizontal axis is a logarithmic time scale.
the $4\pi M$-$\ln r$ data. In the third method, the ZFC flux creep was repeated over a period of about one hour, taking 60 measurements and fitting a straight line to the $4\pi M$-$\ln r$ points for times larger than $\ln|t(s)|=7$, which corresponds to 18.3 minutes. In each of these methods, the initial data point was assigned the initial time of 60 s. This initial time should be the time elapsed from when the sample sees the new field to when the first measurement is taken. There is considerable uncertainty here because the time at which the field is stabilized is not recorded during the automated sequence. Even if it were recorded, the sample still sees a large fraction of this field before the field becomes stable. For this reason, analysis using the initial points was avoided when possible, since the error due to this initial time uncertainty has less effect on the slope of the longer-time points.

A typical comparison of the three methods at $T=6$ K and $\mu_0H=0.1$ T and 0.2 T, $H \parallel c$, is illustrated in Fig. 4.10. The difference in slopes for the two 0.1 T ZFC measurements was 3%, even though the magnetization values were 8% different (perhaps due to a residual field in the 10-point ZFC measurement, since no degaussing was done prior to it). The difference between the creep rate determined from the hysteresis measurement and the 60-point ZFC measurement was about 12%. Such a difference is expected given the different flux profiles arising from different field and temperature histories of the sample in each case. Similar differences are evident in Fig. 4.11 which compares the creep rate methods at $T=4$ K and fields up to 1 T. Figure 4.12 shows the slopes $d(4\pi M)/d(\ln r)$ verses field for temperatures $T=4, 6, 8$ K using the 60-point ZFC creep method. Beyond $\mu_0H=0.1$ T, the creep rate decreases with temperature and field in both orientations, and is significantly smaller for $H \parallel c$.

Hysteresis measurements were used to determine $\Delta M$, the difference between field-decreasing and field-increasing magnetization. The fifth point at each field step during the hysteresis measurement was used to calculate $\Delta M=M_{\text{dec}}-M_{\text{inc}}$. By this time, the
Fig. 4.11  Flux creep rates (slopes $d(4\pi M)/d(\ln t)$) as a function of field obtained using the different methods described in the text for NCCO at $T=4$ K with $H \parallel c$
Fig. 4.12  Flux creep rates in NCCO obtained using 1-hour long ZFC creep measurements at $T=4, 6, 8$ K and (a) $H \parallel c$ and (b) $H \perp c$.
magnetization had relaxed for about 10 minutes, but in all cases \( \Delta M \) was at least 20 times larger than the change in \( M \) due to creep, so \( \Delta M \) is probably known to 5\%. Hysteresis loops for both orientations at \( T=4 \) K are shown in Fig. 4.13. The main feature is that the hysteresis is quite small, even at this low temperature, and, although small, the hysteresis is non-zero at higher fields for \( H || c \). The larger normal-state susceptibility for \( H \perp c \) is also evident in this figure. The intragranular critical current density \( J_c \) was estimated using the Bean model [Bean, 1962, 1964]: 

\[
J_c = \frac{17\Delta M}{r},
\]

where \( J_c \) is in units of A/cm\(^2\), \( \Delta M \) is in emu/cm\(^3\), and \( r \), the average grain radius, is in cm. For this sample, \( r=5 \mu m \) was used. This formula assumes a spherical grain shape and was used here because the individual crystals of the grain-aligned samples were irregularly shaped with no obvious orientation dependence to the grain shape.

Figure 4.14 shows the resulting critical current densities for both orientations. At low fields, \( J_c \) is larger for \( H || c \), but at higher fields the reverse is observed. This is emphasized in Fig. 4.15 showing the crossover in critical current density to larger values for \( H \perp c \) at about \( \mu_0 H=0.25 \) T. The influence of the higher irreversibility line for \( H \perp c \) may be the cause of this \( J_c \) crossover, since the current flow giving rise to the magnetization is expected to be larger in the Cu-O planes, which occurs for \( H || c \), but pinning is expected to be enhanced for \( H \perp c \) at sufficiently high fields.

The flux creep and hysteresis data can be parameterized in terms of the ratio of effective pinning potential \( U_{eff} \) to \( kT \) from the model of Beasley, Labusch, and Webb [Beasley et al., 1969] discussed in Chapter 2: 

\[
\frac{U_{eff}}{kT} = \frac{rJ_c}{30S}.
\]

Here, \( J_c \) is the intragranular critical current density obtained from the hysteresis loops, and \( S \) is the flux creep rate \( S=dM/d(lnr) \). \( U_{eff}/kT \) is plotted as a function of field in Fig. 4.16. There is scatter in the data at larger fields due to the very low \( J_c \)'s, but a decline in \( U_{eff}/kT \) with increasing field is clearly evident. A smooth curve for each temperature was drawn through the points.
Fig. 4.13  Hysteresis loops in NCCO at T=4 K for both $H \parallel c$ and $H \perp c$
Fig. 4.14 Intragranular critical current densities for NCCO derived from the hysteresis data for (a) $\mathbf{H} \parallel \mathbf{c}$ and (b) $\mathbf{H} \perp \mathbf{c}$
Fig. 4.15  Plot of the anisotropy in the intragranular critical current density and the crossover at low fields in NCCO at $T=4$ K
Fig. 4.16  Ratio of effective pinning potential $U_{eff}$ to $kT$ for NCCO obtained from the flux creep and hysteresis data using the Beasley model. (a) $H \parallel c$; (b) $H \perp c$
assuming a monotonic decrease with field, and field and temperature points were obtained for constant values of $U_{\text{eff}}/kT$.

The lines of constant $U_{\text{eff}}/kT$ in the H-T plane, along with $H_{\text{irr}}(T)$ and $H_{\text{c}2}(T)$ are illustrated for $H \parallel c$ in Fig. 4.17. Here $U_{\text{eff}}/kT$ lines are calculated using the creep rates obtained from hysteresis measurements. Below $H_{\text{irr}}(T)$ there is a band in the H-T plane where $U_{\text{eff}}/kT$ gradually rises from a value of about 2, where creep is rapid, to a value of about 20, where pinning becomes more substantial. The curvature of the lines of constant $U_{\text{eff}}/kT$ follow closely the curvature of the irreversibility line. In fact, this similarity suggests that it might be reasonable to think of the irreversibility line as a line of constant $U_{\text{eff}}/kT=1$, where the thermal energy, comparable to the well depth, effectively depins the flux lines. If this were true, the irreversibility line could be thought of as a depinning line or a flux-line lattice melting line.

The anisotropy of NCCO in the H-T plane is illustrated in Fig. 4.18. The lines for $H_{\text{lc}}$ lie at higher temperatures and fields than those for $H \parallel c$. In particular, the $U_{\text{eff}}/kT=2$ line for $H_{\text{lc}}$ lies nearly on top of the $U_{\text{eff}}/kT=10$ line for $H \parallel c$. The larger values of $U_{\text{eff}}/kT$ for $H_{\text{lc}}$ seem to be consistent with the larger irreversibility crossover as well. It appears that deeper effective pinning wells are available and the flux lattice is stiffer when $H_{\perp c}$, at least for the temperatures and fields represented in this diagram.

NCCO and Tl(2223) are two very different superconductors. Tl(2223) [Lichtenberger et al., 1991; Lichtenberger, 1991] is a p-type superconductor with $T_c=120$ K and $\xi_{ab}=1.5$ nm, while NCCO has both electron and hole carriers, a $T_c$ of 24 K, and $\xi_{ab}=5$ nm. They are both highly anisotropic, however. On a reduced temperature scale $t=T/T_c$, the H-T phase diagrams for NCCO ($H \parallel c$) and Tl(2223) are remarkably similar, as shown in Fig. 4.19. Here, the $U_{\text{eff}}/kT=10$ lines nearly coincide, and the transition to flux pinning
Fig. 4.17 Phase diagram in the H-T plane for NCCO with $H \parallel c$
Fig. 4.18 Anisotropy in the H-T phase diagram for NCCO plotted on a reduced temperature scale $T/T_c$. Lines of constant $U_{eff}/kT$ are plotted along with the irreversibility lines for both field orientations.
Fig. 4.19  Comparison of H-T phase diagrams for NCCO and Tl(2223) on a reduced temperature scale $t = T/T_c$. 
behavior occurs in roughly the same window in the H-t plane. This seems to indicate anisotropy may play a more important role in flux pinning than carrier type or coherence distance.

Although the absolute values of $U_{eff}/kT$ depended on whether the creep rate was obtained from hysteresis or ZFC measurements (the difference is about 20%), the conclusions we draw from the analysis are independent of creep rate method, since the relative positions of lines of constant $U_{eff}/kT$ when comparing NCCO $H \parallel c$ and $H \perp c$ (and BKBO, below) are independent of method.

4.2. Magnetization of $\text{Ba}_0.6\text{K}_{0.4}\text{BiO}_3$

$\text{Ba}_0.6\text{K}_{0.4}\text{BiO}_3$ is different from the other high-$T_c$ superconductors in that it has a cubic perovskite crystal structure and no CuO$_2$ sheets, which have such a dramatic impact on the physical properties of the high-$T_c$ cuprates. Like the cuprates, however, $\text{Ba}_0.6\text{K}_{0.4}\text{BiO}_3$ is a doped insulator and has a large $T_c/N^*(0)$ ratio, where $N^*(0)$ is the electronic density of states at the Fermi level [Batlogg et al., 1988]. Magnetization studies were undertaken to compare and contrast this superconductor with the other high-$T_c$ materials.

Magnetization of $\text{Ba}_0.6\text{K}_{0.4}\text{BiO}_3$ (BKBO) was measured both before and after irradiation with neutrons in order to compare the effect of irradiation damage on flux pinning with the other high-$T_c$ materials. The ZFC and FCW M-vs-T measurements before irradiation were taken in temperature steps of 1.0 K, and the sample was mounted in a quartz tube, while those after irradiation were taken in steps of 0.5 K with the sample mounted in a plastic soda straw (due to sample deformation) with GE varnish; all other measurement parameters were the same. The pre-irradiation M-vs-T results suffered from an apparent artifact of the measurement process in that the magnetization values for ZFC and FCW were
slightly different (4x10^{-5} emu at 25 K and 1 T) in regions which surely were reversible. There was also a sudden paramagnetic upturn (as temperature increased) in the normal state region near 40 K which was observed at all fields except the first one of the measurement sequence. This is shown in Fig. 4.20a along with the corresponding M-vs-T measurement taken after irradiation in Fig. 4.20b. It is clear that the post-irradiation measurement is free of these artifacts, which may caused by a small amount condensed oxygen on the surface of the sample, since oxygen undergoes a para-antiferromagnetic transition near 43 K and is strongly paramagnetic above this temperature [Quantum Design, 1991]. Faulty rubber seals on the sample transport system are known to have been one source of this problem in other Quantum Design systems [Quantum Design, 1991]. To attempt to correct for these problems, the background was subtracted by fitting M-vs-1/T above T_c, but below the paramagnetic upturn, for both ZFC and FCW and subtracting the extrapolated fits below T_c. For post irradiation measurements, it was only necessary to fit one or the other of the ZFC and FCW curves, since they were the same within the error of the measurement in the reversible region near T_c, and there was no paramagnetic upturn above T_c. In this case, the average of the ZFC and FCW values were used to minimize the noise. Results of the pre-irradiation background subtraction are shown in Fig. 4.21. Despite the problems with the pre-irradiation data, using the magnetization processed in this way gave qualitatively the same results for the field-dependence of the specific heat jump before and after irradiation.

The irreversibility line for BKBO was obtained by the same method used for NCCO, with the irreversibility temperature defined as the temperature at which ln|ZFC-m_{FCW}|=1x10^{-4} emu. Figure 4.22 shows this line and ln(1-T/T_c)-vs-ln(H_{irr}) which has a slope of 0.64. This is near the value of 0.67 obtained in BKBO by Shi et al. [Shi et al., 1991] and commonly found for Y123 [Malozemoff, 1989], but some caution must be taken given the problems with the measurement described above.
Fig. 4.20  
(a) Moment-vs-temperature data for BKBO at $\mu_0 H = 1$ T both before and after background subtraction. The paramagnetic upturn above 40K is speculated to be due to oxygen condensed on the sample surface. (b) ZFC and FCR $4\pi M$-vs-T curves both before and after neutron irradiation. Pre-irradiation data suffered from a slight shift in the ZFC and FCR curves, but post-irradiation data were free of this artifact.
Fig. 4.21  Pre-irradiation ZFC and FCR magnetization curves for BKBO at $\mu_0H=1$ T after background subtraction
Fig. 4.22  
(a) Irreversibility crossover for BKBO using the 0.1 menu criterion.  
(b) 
Plot of ln(1-T/Tc)-vs-ln(H_{irr}) which gives a slope of 0.64.
4.2.1. Reversible Magnetization of BKBO

The Ginzburg-Landau upper critical field $H_{c2}(T)$ for BKBO was determined by extrapolation from the "linear" M-vs-T region as for NCCO. The M-vs-T data are displayed in Fig. 4.23; the ZFC and FCW values have been averaged. It appears that these data obey the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory better than NCCO or the other high-$T_c$ cuprates in that the slopes $dM/dT$ are nearly constant for fields from 1 T to 5 T. In this case, two different regions were fitted. The first, shown in Fig. 4.23a, was a 3 K region from just above the irreversibility temperature which resulted in an upper critical field slope $dH_{c2}/dT$ of -0.42 T/K, shown in Fig. 4.24. This compares favorably with the value of -0.5 T/K obtained by Batlogg et al. [Batlogg et al., 1988] but is much less than -0.83 T/K, which was observed by Kwok et al. [Kwok et al., 1989]. Kwok et al. fit their magnetization curves in a linear region which was closer to the onset temperature. Although the data presented in our work are not strictly linear over any temperature range, fitting this data in a similar region (a 3 K region ending 2 K below the onset temperature) yields a slope of -0.74 T/K. This is an ambiguous method for determining $H_{c2}$ for this material, since the M-vs-T curves are quite rounded near $T_c$. Beyond the rounding, however, the data are reasonably linear and the slopes $dM/dT$ nearly constant for the 1-5 T data.

The change in free-energy with field and the field-dependence of the specific heat jump were determined for BKBO as described above for NCCO. For BKBO, however, the irreversibility line lies higher in the H-T plane, which limits the region of thermodynamic reversibility. For this reason, $\mu_0H=1$ T rather than zero field was used as a baseline, and we determined $G_H-G_{1T}$ and $C_{1T}-C_H$. As above, the ZFC and FCW values were averaged in order to extend the analysis several Kelvins down in temperature. M-vs-H and $(G_H-G_{1T})$-vs-T results are presented in Fig. 4.25. The $G_H-G_{1T}$ curves show the rounding near $T_c$ and the
Fig. 4.23 (a) M-vs-T curves for BKBO. The background has been subtracted and the ZFC and FCR data averaged. The straight lines are fits to three data points on each curve, where the fitting range spans from 1 K lower than $T_{irr}$ to 2 K higher than $T_{irr}$. (b) Complete set of the data displayed in (a).
Fig. 4.24 Upper critical field for BKBO determined from a linear extrapolation from the M-vs-T data over the range described in the text. Fitting the $H_{c2}(T)$ points from 1-5 T gives a slope $dH_{c2}/dT = -0.42 \, \text{T/K}$. The irreversibility crossover is also displayed.
Fig. 4.25  
(a) M-vs-H data for BKBO transposed from the M-vs-T measurements.  
(b) Free-energy difference with field $G_{H} - G_{T}$ for BKBO
near field independence at lower temperatures characteristic of the copper-oxide superconductors referenced above.

The corresponding $C_{IT} - C_H$ curves are presented in Fig. 4.26a. The sketch in Fig. 4.26b illustrates the quantity derived here. Although this material shows evidence of electron-phonon coupling similar to conventional superconductors [Huang et al., 1990], the field dependence of the specific-heat jump derived in this work is qualitatively very similar to the behavior observed in the high-$T_c$ cuprates; the peak is broadened with increasing field, but the onset of the jump does not shift. This is in direct contrast to the calorimetric measurements made by Graebner et al. [Graebner et al., 1989] in which a 31 K zero-field jump moved unbroadened with increasing field to lower temperatures along the $H_{c2}(T)$ line determined by magnetization measurements. In their experiment, however, the signal-to-noise ratio was extremely small, with the electronic contribution to the specific heat estimated by them to be only about 0.1% of the total measured heat capacity. Their data, as it appeared in Ref. [Graebner et al., 1989] and after subtracting the offset (while preserving the relative heights), are shown along with $C_{IT} - C_H$ from the present study in Fig. 4.27. They obtained a jump $\Delta C_p$ of 0.54 mJ/cm$^3$K. The maximum value of the $C_{IT} - C_{s5.5T}$ curve is 1.8 mJ/cm$^3$K, which sets a lower limit on the value that should be observed in direct calorimetric measurements. Kwok et al. [Kwok et al., 1989] derived $\Delta C_p = 2.37$ mJ/cm$^3$K from magnetization measurements on the temperature dependence of the upper critical field.

Using calorimetric measurements, Hundley et al. [Hundley et al., 1989] and Stupp et al. [Stupp et al., 1989] did not observe a jump near $T_c$. Clearly, it would be of interest to reproduce these measurements on higher quality samples (large single crystals) to determine which type of behavior is intrinsic to this material. Although the measurements here suffered from the experimental artifact described above, measurements taken after
Fig. 4.26 (a) Field-dependence of specific heat in BKBO referenced to $\mu_0H=1$ T. The behavior is qualitatively similar to other high-Tc cuprates. (b) Schematic diagram illustrating the quantity being plotted in (a)
Fig. 4.27  
(a) Direct, calorimetric specific heat data on BKBO from Graebner et al. showing the resulting data after extracting the electronic contribution from the total specific heat.  (b) Comparison of the results $C_{IT}-C_{H}$ from the present study with the zero-field result $\Delta C_p$ of Graebner et al. We have subtracted the offset while preserving the relative height of the calorimetric data. The zero-field jump $\Delta C_p$ corresponds to $C_0-C_{He2}$.
did not suffer from such artifacts and showed the same qualitative behavior as the pre-irradiation measurements. This work will be described in detail below.

4.2.2. Irreversible Magnetization of BKBO

In an attempt to learn the role of anisotropy in flux pinning [Kes et al., 1990; Palstra et al., 1991; Hao and Clem, 1991b], hysteresis and flux creep were measured and analyzed for the isotropic BKBO in a manner similar to that described above for NCCO. The Bean model was used to estimate $J_c$ from hysteresis loops, and the Beasley model was used to estimate an effective pinning potential.

Hysteresis loops for $T=5$ and $15 \text{ K}$ are illustrated in Fig. 4.28, and the resulting critical current densities plotted in Fig. 4.29. Hysteresis loops for BKBO were measured by applying a field (in direct mode) of $-5 \text{ T}$, holding for 10 minutes, removing the field and then applying a series of positive fields up to $5.5 \text{ T}$ and back to zero. At each field, the magnetization was measured 11 times in succession. The same Bean-model formula $J_c = 17AM/r$ used for NCCO was used for BKBO; $r=5 \mu \text{m}$ was used for this sample. The last point in the creep sequence at each field was used to calculate $\Delta M$. The critical current densities of BKBO were an order of magnitude larger than those of the very weak pinning NCCO ($3 \times 10^5 \text{ A/cm}^2$ at $T=5 \text{ K}$ and $\mu_0H=1 \text{ T}$ for BKBO compared to $3 \times 10^4 \text{ A/cm}^2$ at $T=4 \text{ K}$ and $\mu_0H=1 \text{ T}$ perpendicular to $c$ for NCCO). BKBO $J_c$'s were smaller, however, than those observed in single-crystal Y123 ($>1 \times 10^6 \text{ A/cm}^2$ at $T=5 \text{ K}$ and $\mu_0H=1 \text{ T}$ [Sauerzopf et al., 1990]).

Two methods of measuring flux creep in BKBO were used: the hysteresis loop method and the ZFC creep method. In the hysteresis method, magnetization was measured 11 times in about 12 minutes at each successive field step. A slope was determined by fitting the last 5 out of 11 points of the $4\pi M$-vs-$lnr$ data with a straight line. In the ZFC
Fig. 4.28  Hysteresis loops for BKBO at (a) T=5 K and (b) T=15 K
Fig. 4.29 Intragranular critical currents derived from hysteresis loops
measurements, the sample was cooled from above $T_c$ to the measuring temperature, the field applied in direct mode, and the magnetization measured 60 times over approximately 65 minutes. A comparison of the two flux-creep methods is shown for $T=5$ K and $\mu_0H=0.1$ and 1.0 T in Fig. 4.30. The ZFC $4\pi M$-vs-$\ln t$ measurements are relatively linear, but the hysteresis data are initially non-linear and approach linearity over time. The slope obtained by fitting the final 5 (out of 11) points of the hysteresis data to a straight line is 30% larger than the value obtained by fitting a straight line to the ZFC points for times larger that $\ln[t(s)]=7$. As discussed above, these two different measurement techniques create different initial flux profiles in the sample. In addition, there is more uncertainty in the time of the initial measurement in the hysteresis measurement. In this method the initial measurement was assumed to take place 60 s after setting the magnetic field. In the ZFC measurement, an external device control (EDC) program was used to control the measurement sequence, and the initial time could be recorded directly, since the time at which the magnet became stable was also available. Of course, since the magnet takes a finite time to stabilize, the sample is exposed to a field approaching the desired value for several seconds before stabilization occurs. Figure 4.31a shows flux creep data from the 5 K hysteresis loop for $\mu_0H=0.1$ T in which three different values of the initial time $t(i)$ were tried. It is evident that the uncertainty in the initial time has the largest effect on the creep rate (or slope) at shorter times, but if the last 5 (out of 11) points were fit to a straight line, only a 5% difference in creep rate for $t(i)=45$ s and $t(i)=75$ s was obtained.

Figure 4.31b compares the creep rates obtained via the two methods at $T=5$ K. At low fields, the data follow the same trend of decreasing flux creep rate with field; the monotonicity of the decrease in creep rate with increasing field for the ZFC data indicate that $\mu_0H^*$ is less than 0.1 T for this sample. The ZFC data have more scatter at higher fields due to the occurrence of flux jumps, which made the fitting more difficult. An example of a flux
Fig. 4.30 Comparison of flux creep methods for BKBO at T=5 K and a field of (a) 0.1 T and (b) 1.0 T
Fig. 4.31  (a) Effect of starting time \( t(i) \) uncertainty in the hysteresis flux creep measurements on BKBO at \( T=5 \) K and \( \mu_0 H=0.1 \) T. (b) Comparison of creep rates obtained from ZFC and hysteresis measurements on BKBO at \( T=5 \) K.
jump is shown for T=5 K and \( \mu_0 H = 4 \) T in Fig. 4.32a. The analysis to obtain \( U_{\text{eff}}/kT \) was carried out on the both the hysteresis data and ZFC creep data in order to determine the severity of the differences in the H-T plane. The corresponding H-T phase diagram derived from the ZFC creep data is plotted along with the results from hysteresis creep in Fig. 4.32b. Despite an average difference of about 20% in \( U_{\text{eff}}/kT \) values, this difference does not affect the conclusions of this section, i.e., the lines are shifted only relatively little compared to the difference in the position of the lines for the different superconductors compared.

Effective pinning potentials were derived from the hysteresis creep measurements in order to determine the position of lines of constant \( U_{\text{eff}}/kT \) in the H-T plane and compare them to the corresponding lines in other high-Tc materials. From the hysteresis measurements, the increasing-field and decreasing-field creep rates were averaged. The magnitude of the creep rates were quite similar, as shown in Fig. 4.33; this was also observed in Pb alloys by Beasley et al. [Beasley et al., 1969]. The field dependence of the average creep rate is illustrated in Fig. 4.34a, and is shown to be reproducible for T=5 K in Fig. 4.34b. This creep data was combined with the critical current data of Fig. 4.29 to derive \( U_{\text{eff}}/kT \)-vs-H curves shown in Fig. 4.35a. Smooth curves were drawn through the \( U_{\text{eff}}/kT \)-vs-H data, and lines of constant \( U_{\text{eff}}/kT \) in the H-T plane, presented in Fig. 4.35b, were obtained as described for NCCO. \( U_{\text{eff}}/kT \) rises relatively quickly from a value of 20 to 100 below the irreversibility crossover \( H_{\text{irr}}(T) \).

To examine the possible effects of anisotropy on pinning [Kes et al., 1990; Palstra et al., 1991], the effective pinning potentials of NCCO and BKBO were compared. NCCO has a tetragonal crystal structure with layered CuO\(_2\) planes and BKBO is cubic, but they have similar Tc's and \( \xi \)'s. Figure 4.36 reveals that the NCCO sample has a much smaller irreversible region and weaker pinning than BKBO. Lines of constant \( U_{\text{eff}}/kT \) for BKBO rise more quickly below the irreversibility crossover, with \( U_{\text{eff}}/kT \) for BKBO exceeding 40 even
Fig. 4.32  (a) Flux jump in BKBO during ZFC creep at T=5 K and $\mu_0 H=4$ T. (b) Comparison of the results of constant $U_{\text{eff}}/kT$ in the H-T phase diagram when the creep rates are derived from ZFC creep as opposed to hysteresis creep. The difference shown here does not affect the conclusions of this section.
Fig. 4.33  Flux creep rates for increasing and decreasing fields during hysteresis measurements at (a) 5 K and (b) 20 K
Fig. 4.34  (a) Average of creep rates for increasing and decreasing-fields during a hysteresis loop for BKBO. (b) Reproducibility of hysteresis creep rates at T=5 K
Fig. 4.35  (a) $U_{\text{eff}}/kT$-vs-field for BKBO. (b) The resulting lines of constant $U_{\text{eff}}/kT$ in the H-T plane for BKBO
Fig. 4.36  Comparison of H-T phase diagram for NCCO and BKBO
above the irreversibility line for NCCO (H $\parallel$ c). The large anisotropy of NCCO may weaken flux pinning in this material [Palstra et al., 1991]. It may also be possible to attribute the difference in activation energies to the extrinsic defect structure, but that variable was not systematically tested in this work.

4.2.3. Neutron Irradiation Effects

The BKBO sample described above was irradiated with neutrons in order to learn more about the factors controlling pinning in this material. Fast neutrons (E $>$ 0.1 MeV) from the TRIGA Mark-II nuclear fission reactor in Vienna, Austria irradiated the sample with a total fluence of $1 \times 10^{22}$ neutrons m$^{-2}$. The energy spectrum of the reactor is illustrated in Fig. 4.37. The flux density of fast neutrons (E $>$ 0.1 MeV) is $7.6 \times 10^{16}$ m$^{-2}$s$^{-1}$ at full power [Sauerzopf et al., 1991]. The sample was enclosed in a quartz tube containing pure He during the 36 h of irradiation. Following irradiation, the sample had become brittle and somewhat deformed, with the cylinder diameter increasing from 3.4 to 3.9 mm due probably to the large neutron cross section of the epoxy and the concomitant damage.

The amount of flux excluded after irradiation remained nearly the same, as the low-field M-vs-T curves of Fig. 4.38 show for $\mu_0H=1$ mT and as shown in Fig. 4.39 for $\mu_0H=0.5$ T. This indicates that the neutron irradiation did not cause significant bulk damage to the superconductor (the sample consists of grains electrically isolated by epoxy). A change in $T_c$ of 1 K or less was observed after irradiation.

Comparison of ZFC magnetization measurements at 1 mT, shown in Fig. 4.38, indicates that the onset-$T_c$ decreased by less than 1 K after irradiation. Pre-irradiation measurements were taken only in 1 K temperature intervals, so it is difficult to determine changes of less than 1 K. This small change in $T_c$ is consistent with the work of Thompson et al. [Thompson et al., 1990], who observed a decrease of $T_c$ with fast neutron irradiation of polycrystalline BKBO.
Fig. 4.37  Energy spectrum of TRIGA MARK-II reactor in Vienna
Fig. 4.38  (a) Comparison of low field (1 mT) ZFC magnetization before and after neutron irradiation dose of 1x10^{22} n m^{-2}. T_c changes by 1 K or less as shown in (b)
Fig. 4.39  Comparision of ZFC and FCR curves at 0.5 T after irradiation
of -4 K/10^{23} \text{ n m}^{-2}. Since the fluence in this study an order of magnitude less, a change in $T_c$ of less than 1 K is reasonable. This behavior is much different than in Y123, where a change in $T_c$ with neutron irradiation of -27 K/10^{23} \text{ n m}^{-2} has been observed [Willis et al., 1988], but is similar to what is seen in A15 compounds [Seedler et al., 1978].

To investigate the changes in $H_{\text{irr}}(T)$ and thermodynamic quantities following irradiation, ZFC and FCW $M$-vs-$T$ measurements with a 0.5 K temperature interval were taken over a field range of 0.5 to 5 T after irradiation to match the measurements done prior to irradiation, the only difference being the smaller temperature interval and the sample being mounted in a plastic drinking straw rather than a quartz tube. Using the same criterion as before, the irreversibility crossover was shifted by 2-3 K to higher temperatures following irradiation, as shown in Fig. 4.40. The crossover still behaves approximately as $(1/T/T_c) \propto H_{\text{irr}}^{2/3}$. As stated in section 4.2, some caution must be applied when comparing the irreversibility lines due to the experimental problem with the pre-irradiation measurements.

The magnetic-field dependence of the post-irradiation free-energy difference, $G_H - G_{1T}$, and specific heat jump $C_{1T} - C_H$ were derived as before from the data in the reversible region of the $H$-$T$ plane. The magnetization was obtained from the raw data in the following way. First, the magnetization values for ZFC and FCW were averaged; the averaged values were fitted with a straight line to $4\pi M$-vs-$1/T$ over the normal state temperature range of 29-35 K, as expected for Curie's law. The $1/T$ fit was extrapolated from 29 K to 10 K and subtracted from the average values. This background subtraction is depicted in Fig. 4.41. The processed $M$-vs-$T$ data are illustrated in Fig. 4.42, and the post-irradiation free-energy data compared directly to the pre-irradiation results in Fig. 4.43. It can be seen from this figure that the post-irradiation values of $G_H - G_{1T}$ are decreased by about 20% at low temperatures relative to the values prior to irradiation. The post-irradiation $C_{1T} - C_H$ curves are compared with the pre-irradiation data in Fig. 4.44. The behavior of $C_{1T} - C_H$ is
Fig. 4.40  (a) Comparision of BKBO irreversibility crossover after irradiation. (b) log-log plot
Fig. 4.41  (a) Background subtraction for BKBO after irradiation. (b) enlargement of (a)
Fig. 4.42 Post-irradiation M-vs-T curves for BKBO
Fig. 4.43  Comparison of free-energy difference in BKBO after irradiation
Fig. 4.44  (a) Comparison of field-dependent specific heat for BKBO before and after irradiation
qualitatively the same before and after irradiation. Post-irradiation curves are shifted approximately 1 K downward in temperature and the peak values are suppressed by about 20% at $\mu_0 H=5$ T.

Hysteresis decreases slightly (approximately 10%) after the $1 \times 10^{22}$ n m$^{-2}$ fluence of fast-neutron irradiation as shown in Fig. 4.45. To compare flux pinning after irradiation with the virgin sample, hysteresis measurements were taken at $T=5$, 10, 15, and 20 K using the same measuring sequence as before. No increase in hysteresis was observed at any field in these measurements. A similar insensitivity of $J_c$ on fast-neutron irradiation in polycrystalline BKBO was observed by Thompson et al. [Thompson et al., 1990] for fluences up to $1.4 \times 10^{22}$ n m$^{-2}$. This is much different than what is observed in Y123, where $\Delta M$ increased by a factor of 3 or more with similar fluences [Sauerzopf et al., 1991]. It is not understood at present why pinning in BKBO is insensitive to this fluence of fast neutrons, although elementary considerations [Campbell and Evetts, 1972] would suggest that the size of the defects produced by the neutrons in this material is not compatible with the core size of the vortices, since optimal pinning occurs when the two sizes are approximately equal. No microscopic investigations using transmission electron microscopy (TEM) have been done to determine the characteristics of the radiation damage in this material.
Fig. 4.45 Hysteresis curves before and after irradiation in BKBO for T=5 and 20 K
Magnetization measurements on \( \text{Ba}_{0.8}\text{K}_{0.4}\text{BiO}_3 \) (BKBO) and grain-aligned \( \text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{4-x} \) (NCCO) have been carried out in order to study the reversible and irreversible behavior in the field-temperature plane and compare the results with conventional superconductors and other high-\( T_c \) superconductors. NCCO is unique among the high-\( T_c \) cuprates in that it has electron carriers as well as holes. BKBO is unique because it is isotropic and has no \( \text{CuO}_2 \) layers.

Thermodynamic quantities were derived from the reversible magnetization. For NCCO, free-energy curves \( G_H-G_0 \) were found to be qualitatively similar to the \( \text{Y-Ba-Cu-O} \) and \( \text{Tl-Ba-Ca-Cu-O} \) cuprates in that there was a rounding of the \( (G_H-G_0) \text{-vs-} T \) curves near \( T_c \) followed at lower temperatures by a nearly temperature-independent slope. The field-dependence of the specific heat jump, \( C_0-C_H \), also had the qualities similar to the high-\( T_c \) cuprates such as peak broadening with increasing field and a field-independent onset temperature. The value at the highest available field, \( C_0-C_{2T} = 1.2 \text{ mJ/cm}^3\text{K} \), establishes a lower limit of the calorimetric specific heat jump \( \Delta C_p \).

An irreversibility crossover \( H_{irr}(T) \) was determined from the splitting of the ZFC and FCR magnetization curves. For NCCO, the relation \( (1-T_{irr}/T_c) \propto H^{0.3} \) was observed for both field orientations, but for \( \text{H} \perp \text{c} \) the \( H_{irr}(T) \) crossover was shifted to higher temperatures and fields. There was a wide region of reversible behavior for both orientations. Below the irreversibility line, hysteresis and flux pinning were observed. The intragranular critical current densities determined from the Bean model showed an anisotropy, with \( J_c \) larger for \( \text{H} \parallel \text{c} \) at low fields, but larger for \( \text{H} \perp \text{c} \) at higher fields. Flux creep and hysteresis data were parameterized in terms of a single effective pinning potential \( U_{eff} \) in order to study the crossover from reversible to flux-pinning behavior in this material. There is a band in the H-
T plane below $H_{irr}(T)$ where $U_{eff}/kT$ gradually rises from 2 to 20. These lines of constant $U_{eff}/kT$ are shifted to higher temperatures for $H_{irr}$, consistent with the difference in $H_{irr}(T)$. The position of the $U_{eff}/kT$ lines for NCCO are in approximately the same location as those for Tl(2223), when a reduced temperature scale is used. Since Tl(2223) is a hole-carrier material with a much smaller coherence distance than NCCO, anisotropy may be more important than carrier type or coherence distance in determining pinning strength in these materials, since both materials are highly anisotropic.

Magnetization-vs-temperature (M-vs-T) data for BKBO was found to be similar to that expected from the standard Ginzburg-Landau treatment in that there were sections of the M-vs-T curves in which the slopes $dM/dT$ were nearly constant for increasing fields. This is in contrast to the situation in Y123 and NCCO where $dM/dT$ varies with field. Rounding of the M-vs-T curves near $T_c$ is still observed, however. In this reversible region, the free energy curves $(G_H-G_{1T})$-vs-$T$ exhibit the features found in the other high-$T_c$ materials. The specific heat jump values $C_{1T}-C_H$ derived from the free energy curves are also qualitatively similar to the high-$T_c$ cuprates, in contrast to the results of one set of direct measurements on single crystals of BKBO [Graebner et al., 1989]. In the present study, the onset temperature is constant in field, and the peak broadens as field is increased. A maximum value of $C_{1T}-C_{ST} = 1.8 \text{ mJ/cm}^3\text{K}$ sets a lower limit on the value of $\Delta C_p$, compared to the Graebner value of $0.54 \text{ mJ/cm}^3\text{K}$ [Graebner et al., 1989].

The irreversibility crossover for BKBO was obtained from the M-vs-T splitting and found to obey $(1-T_{irr}/T) \propto H^{0.64}$. This power of 0.64 is close to the value of $2/3$ observed for Y123. The reversible region of the H-T plane is smaller for BKBO than for NCCO. As in the case of NCCO, flux creep and $J_c$ data were parameterized in terms of $U_{eff}/kT$. $U_{eff}/kT$ rises relatively quickly from 20 to 100 below the irreversibility crossover, compared to the
more gradual increase in $U_{\text{eff}}/kT$ for NCCO. BKBO has a smaller reversible region and stronger effective flux pinning potentials than NCCO.

Fast-neutron irradiation of BKBO with a fluence of $1 \times 10^{22}$ n m$^{-2}$ did not increase critical current density in this sample. There was a small ($< 2$ K) shift in temperature in the $(C_{\text{IT}} - C_{\text{H}})$-vs-$T$ data, but the qualitative features of this thermodynamic data remained intact following the irradiation.
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Terry Holesinger deserves special recognition, since we became friends at the beginning of graduate school, and he listened to me complain for many years. Karl Lichtenberger also deserves thanks for his help during this time. Other people in the department also offered their friendship: Junho Gohng, Qiang Qian, Ming Xu, Junghyun Sok, Ted Miller, Kelly Roos, Ann Bouchard, and Kevin Jacobs, to name a few. To them I am very grateful.

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