# Flux creep in a polycrystalline $Ba_{0.6}K_{0.4}BiO_3$ superconductor

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Magnetization curves have been measured as a function of temperature for a polycrystalline sample of $Ba_{0.6}K_{0.4}BiO_3$. These measurements reveal significant reversibility at modest fields for all temperatures studied. The irreversibility line $(H^*, T^*)$ is determined for this material and shows that $H^*$ is less than 0.8 T at all temperatures. The logarithmic magnetic relaxation rate $A = dM/d\ln(t)$ has been studied for this material, as a function of both field and temperature. Analysis using the flux-creep model reveals the average pinning energy $U_0$ to be $0.08 \pm 0.02$ eV. This extremely small pinning energy is used to explain the small critical current, its strong dependence on field, and the significantly reversible behavior in this material.

The $Ba_{0.6}K_{0.4}BiO_3$ superconductor is of current topical interest because it is a non-copper-containing oxide superconductor with a $T_c$ near 30 K.[1,2] This system is also of interest because it is three dimensional, by virtue of its cubic structure, and because of its structural similarity to the $Ba(Pb,Bi)O_3$ family of superconductors. Further, this system offers yet another oxide superconductor from which to glean information as to fundamental and technical properties of this class of materials.

In this paper we report magnetic properties of $Ba_{0.6}$-$K_{0.4}BiO_3$, which was chosen because it has the highest $T_c$ (29 K) in the series $Ba_{1-x}K_xBiO_3$.[1] Our sample is single phase, shows a sharp magnetic transition at 29 K and is considered to be of very high quality. Magnetization data show the sample to exhibit nearly reversible properties for all but the lowest temperatures and fields ($< 5$ K and $< 0.8$ T). This reversibility is consistent with small values of the critical current density as calculated from the Bean model. The critical current density can also be observed to have a very rapid drop off with applied field. Both of these observations are consistent with very weak pinning in the material. We have further examined the nature of the pinning using magnetic relaxation measurements from which the average pinning energy can be deduced using the flux-creep model. These measurements confirm that the pinning energy is indeed extremely small and similar to that measured in other bismuthate superconductors.[3]

The $Ba_{0.6}K_{0.4}BiO_3$ was prepared using a simplified synthetic route.[4] We ground, pelletized, and baked overnight at 700 K stoichiometric amounts of $BaNO_3$ and $Bi_2O_3$. This mixture was then added to an appropriate quantity of $KNO_3$, pelletized, baked, and annealed following the procedures described by Hinks et al.[5,6] The pellets were first baked at 700 °C for 1 h in flowing $N_2$, and sequentially annealed at 450 °C for 3 h and 375 °C for 4 h before furnace cooling, all in flowing $O_2$. The sample used in these experiments was a thin slice, approximately 1 mm thick at the center, cut from the edge of one of the pellets. An x-ray-diffraction scan of the surface of the pellet showed it to be cubic ($Im3m$) and single phase with a lattice constant of 4.2869 Å at 297 K. Subsequent neutron-diffraction studies[7] of the powdered pellets showed that a small amount of the second monoclinic phase ($I2/m$) was

present. Presumably, the latter was an oxygen deficient $Ba_{1-x}K_xBiO_y$, resulting from incomplete oxygenation of dense interior portions of the pellet that were produced from liquid-phase sintering of the nitrates. Rietveld refinements of the structure of the superconducting cubic phase on two separate sets of neutron-diffraction data gave an average stoichiometry of $Ba_{0.59}K_{0.41}BiO_{3.03}$.

dc susceptibility measurements were made using a Quantum Design superconducting quantum interference device (SQUID) magnetometer in a field of 50 Oe. These measurements reveal a 29-K onset, a 26-K midpoint, and 98% of $4\pi\chi$ flux exclusion at 5 K. Values of the critical current density were determined using the Bean model[8] $J_c = 15\Delta M/R$ where $\Delta M$ is the hysteresis in gauss, $R$ is a typical particle size in cm, and $J_c$ is in $A/cm^2$. This expression yields $\sim 3 \times 10^5$ $A/cm^2$ for our material at 5 K in zero field. Magnetometer magnetization $M$ versus magnetic field $H$ loops were made at 5, 10, 15, 20, and 25 K in maximum fields of up to 2 T, a field large enough to determine the irreversibility limit at all temperatures. An asymptotic field ramping mode is employed so that field history deviations do not exceed $\sim 10$ G.

Magnetization versus time measurements were made, also with the Quantum Design SQUID magnetometer. The procedure for acquiring the magnetic relaxation data consisted of cooling in zero field (ZFC) and, after waiting to attain a stable temperature, application of the field. The first magnetization point was taken after the 3 min required to latch the field. Subsequent magnetization points were taken every 2 min for the duration of the experiment which was typically 1 h. Between runs the field was removed and the sample heated to above its transition temperature to expel all remaining flux. The equilibrium magnetization values ($M_{eq}$) were approximated as the magnetization of a slowly field-cooled (FC) sample at the temperature in question. It was ascertained that negligible relaxation occurred from this field-cooled state.

Figure 1 illustrates typical magnetization curves as a function of increasing and decreasing applied field for temperatures of 5, 10, 15, 20, and 25 K. These curves are significant in their reversibility. For example, even at 5 K, the magnetization curve is essentially reversible for fields greater than 0.8 T. This low-temperature irreversibility

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limit occurs at fields an order of magnitude smaller than those observed for the 1:2:3 materials.[9] This is consistent with the smaller $J_c$'s which can be inferred from the Bean model in these materials and indicative of much weaker pinning. Also indicated is a dramatic fall-off of $J_c$ with applied field in that the irreversibility limit represents the field at which $J_c$ can essentially be taken to be zero.

The irreversibility line can be estimated from these data as is shown in Fig. 2(a). This curve illustrates the "phase boundary" denoted by the locus of points $H^*$-$T^*$ which separates regions of hysteretic response from regions of reversible response in the manner originally prescribed by Müller, Takashige, and Bednorz.[10] Again the significant feature of this curve is the fact that $H^*$ does not exceed 0.8 T at any temperature. Figure 2(b) shows the temperature dependence of the magnetic hysteresis $\Delta M$, at fields of 0, 0.5, 1,2, and 4 kG. The temperature dependence of $\Delta M$ and $J_c$ scale in the Bean model. Note the similarity in the temperature dependence of $\Delta M(T)$ and $H^*(T)$ in Figs. 2(a) and 2(b). Figure 2(c) shows the magnetic hysteresis to scale with $(1-t)^{3/2}$ for all but the lowest temperatures and fields in these materials. This observation is consistent with the assertion that the critical current density is dramatically influenced by thermal activation.[11] The fact that the irreversibility criterion is so manifest in the temperature dependence of the critical current density is a signature of the extremely weak pinning in this material. This result is not surprising in light of significantly smaller values of $J_c$ reported in other bismuthate super-

conductors.[12] This observation has been used to explain anomalous dissipation effects[12,13] in these materials. The small critical current densities are reflected in small driving forces for flux creep and have recently been discussed in terms of a thermally assisted flux flow (TAFF) model by Kes et al.[14]

Magnetic relaxation measurements have now been made on a variety of oxide superconductors.[11,15,16] The flux creep formalism has been used to extract volume pinning energies for these materials. Figure 3(a) illustrates typical time dependences of the magnetization at various temperatures for our $Ba_{0.6}K_{0.4}BiO_3$ sample, cooled initially in zero field, when a field of 1 kG is applied. The magnetization $M$ in each case is normalized by the initial magnetization value $M_1$ as given by the first measured data point ($t_1 = 200$-$250$ sec). The magnetization is seen to change by approximately 2.5% at 20 K within a 1-h measurement period. This is to be contrasted with the case of $YBa_2Cu_3O_{7-x}$ samples in which the relative change was 15% at 40 K,[16] a value comparable to that reported for single crystals of $YBa_2Cu_3O_{7-x}$.[11] For a polycrystalline Tl-2:2:2:3 material the change was over 20% at 70 K. Certainly, the behavior of the $Ba_{0.6}K_{0.4}BiO_3$ sample is not consistent with the so called "giant flux creep" previously reported in $YBa_2Cu_3O_{7-x}$ (Refs. 11 and 15) and Tl 2:2:2:3.[16] This observation points to the fact that even at fields as low as 1 kG, the low driving force regime is approached for these materials.

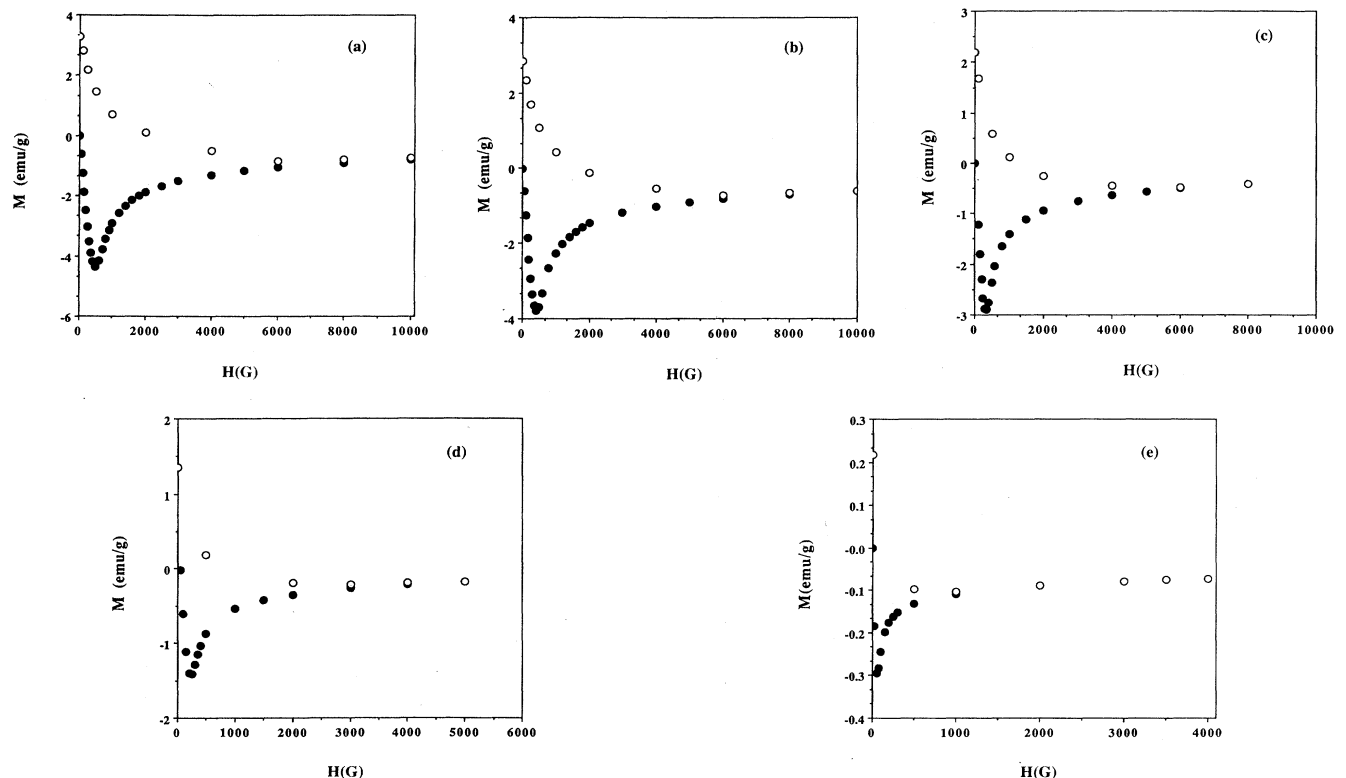In the flux creep model[17] the thermally activated hop-



FIG. 1. Magnetization curves for $Ba_{0.6}K_{0.4}BiO_3$ on increasing (filled circles) and decreasing (open circles) fields for (a) 5 K, (b) 10 K, (c) 15 K, (d) 20 K, and (e) 25 K.
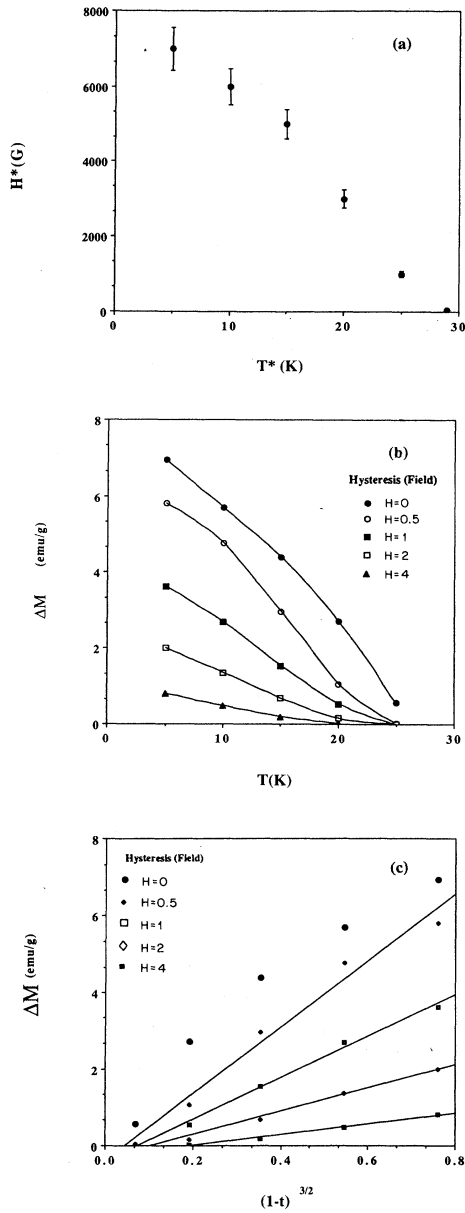
FIG. 2. (a) Irreversibility line $H^*$ vs $T^*$ as determined from hysteresis curves. (b) Hysteresis in the magnetization $\Delta M = M^+ - M^-$ for fixed field as a function of temperature: ●, 0 G; ○, 0.5 G; ■, 1 G; □, 2 G; ▲, 4 G. (c) Hysteresis as a function of $(1-t)^{3/2}$: ●, 0 G; ◆, 0.5 G; □, 1 G; ◇, 2 G; ■, 4 G.
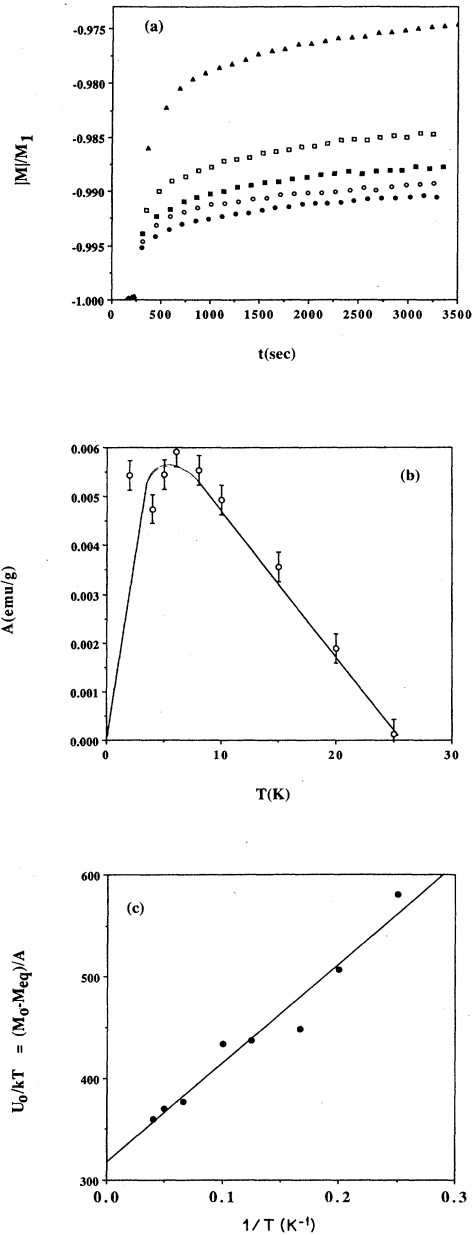


FIG. 3. (a) $M(t)$ as a function of temperature: ●, 2 K; ○, 4 K; ■, 6 K; □, 15 K; ▲, 20 K. (b) Logarithmic relaxation coefficient $A = dM/d\ln(t)$ and (c) Arrhenius plot of $U_0/kT$ vs $1/T$ for the Ba$_{0.6}$K$_{0.4}$BiO$_3$ material.

ping rate for fluxons is expressed as

$$R = R_0 \exp\left[\frac{-U_0}{kT}\right] \sinh\left[\frac{-\Delta W}{kT}\right], \qquad (1)$$

where $U_0$ represents the average pinning energy in the material, $R_0$ is an attempt frequency, and $\Delta W$ is the driving force due to the flux gradient which is proportional to the critical current density of the matrial. In the case of a substantial $\Delta W$ term $\sinh(-\Delta W/kT) \sim \exp(-\Delta W/dT)$. In this limit the time dependence of the magnetization can

be shown to be logarithmic. However, in the case where $\Delta W$ is small, $\sinh(-\Delta W/kT) \sim (-\Delta W/kT)$, and nonlogarithmic time dependence of the magnetization can be derived. In this work we examine the time dependence of the magnetization for a field of 1 kG which is small enough to give a large enough driving force to use logarithmic fits to the time dependence. For low temperatures and fields, our magnetic relaxation data here is accurately described by the empirical relationship

$$M = M_0 + A\ln(t), \qquad (2)$$

which is the hallmark of the flux creep model. This expression is not particularly accurate for high fields and high temperatures (i.e., for very small driving force). This regime will be discussed in a subsequent work.

The very strong temperature dependence of the relaxation in this $Ba_{0.6}K_{0.4}BiO_3$ sample is manifested in the behavior of the derivative of $M(t)$ with respect to $\ln(t)$ as a function of temperature, as illustrated in Fig. 3(b). In the flux creep model this temperature dependence is a manifestation of the temperature dependence of the volume pinning energy $U_0$ divided by the temperature dependent critical current density as given in the following expression:

$$A = \frac{d(M(t) - M_{eq})}{d\ln(t)} = \left[\frac{kT}{U_0}\right]\frac{J_c R}{4c} = \left[\frac{kT}{U_0}\right](M_0 - M_{eq}).$$

$$(3)$$

$J_c$ is related to the maximum value of the nonequilibrium magnetization and $R$ is the thickness of a slab shaped grain. The values of the logarithmic derivative for this sample is more than an order of magnitude smaller than those reported for Tl 2:2:2:3 and Y 1:2:3.[16] The peak in the $A$ vs $T$ curve also occurs at a significantly lower absolute temperature than that of the previously studied materials at comparable fields, signifying that the pinning energy is indeed smaller in these materials.

The average pinning energy $U_0$ can be derived from the temperature dependence of $A$ and $M_0 - M_{eq}$, through an Arrhenius plot of $(M_0 - M_{eq})/A$ vs $1/T$. Here $M_0$ is taken as the fitted value given by Eq. (1) at a reference time of 1 sec and $M_{eq}$ is estimated by the value of the field-cooled magnetization from which no significant relaxation occurs. Such an Arrhenius plot is shown in Fig. 3(c) for the relaxation data of our sample, taken in an applied field of 1 kG. The slope of this curve reveals an activation energy of $0.08 \pm 0.02$ eV for this material. This value of the volume pinning energy is the smallest reported to date in oxide superconductors.

It is interesting to compare the values of pinning energies derived from flux creep measurements in the previously examined polycrystalline samples of Y 1:2:3 and Tl 2:2:2:3 (Ref. 16) and the presently reported $Ba_{0.6}K_{0.4}BiO_3$ sample. The $Ba_{0.6}K_{0.4}BiO_3$ material has a significantly lower-volume pinning energy than either of the previously studied materials. This small pinning energy is interesting in light of the anomalous dissipation effects and small critical current densities observed in the bismuthate superconductors in general. It should also be noted that the Y 1:2:3 material is known to have copious defects in the form of twin boundaries[18] while the Tl 2:2:2:3 material is known to exhibit interesting structural modulation along the $c$ axis due to stacking imperfections.[19] It is therefore plausible that in comparing the volume pinning energies of different oxide materials that extrinsic pinning due to defects may be playing an important role. On the other hand, because of the larger coherence lengths (much larger than the lattice constant) for the $Ba_{0.6}K_{0.4}BiO_3$ material intrinsic pinning is less likely to be an important consideration in these materials. It therefore remains to be seen whether the different pinning energies observed for different oxide superconductors is in any way reflective of their intrinsic pinning properties.

Magnetization measurements as a function of temperature, for a polycrystalline sample of $Ba_{0.6}K_{0.4}BiO_3$, reveal significant reversibility at modest fields for all temperatures. An irreversibility line has been determined with $H^*$ values an order of magnitude smaller than for Y 1:2:3 at similar reduced temperatures. The logarithmic magnetic relaxation rate $A = dM/d\ln(t)$ has been studied for this material, as a function of both field and temperature. Analysis using the flux creep model reveals the average pinning energy $U_0$ to be $0.08 \pm 0.02$ eV for an applied field of 1 kG. This extremely small pinning energy is consistent with the small critical currents and significantly reversible behavior in this material.

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