

Properties of large area $\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films deposited by ionized cluster beams

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$\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$ films have been produced by simultaneous deposition of Er, Ba, and Cu from three ionized cluster beam (ICB) sources at acceleration voltages of 0.3–0.5 kV. Combining ozone oxidation with ICB deposition at 650 °C eliminated any need of post anneal processing. The substrates were rotated at 10 rotations per minute during the deposition which took place at a rate of about 3 to 4 nm. $\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$ films with areas up to 70 mm in diameter have been made by ICB deposition. These films, 100-nm thick, were deposited on SrTiO_3 (100) substrates at 650 °C in a mixture of 6 at. % O_3 in O_2 at a total pressure of 4×10^{-4} Torr. They had T_c ranging from 84.3 to 86.8 K over a 70 mm diameter and J_c above 10^6 A/cm² at 77 K. Another set of three samples, deposited within a 50 mm diameter, was examined by magnetization measurements. These samples had J_c ranging from 8.2×10^6 to 1.1×10^7 A/cm² at 4.2 K and from 2.4×10^5 to 5.1×10^5 A/cm² at 70 K. X-ray diffraction measurements of the three samples showed preferential c -axis orientation normal to the substrate surface. Rocking curves showed small variation in grain misorientation with sample position relative to the center of the substrate holder. Scanning electron micrographs (SEM) of the three samples also show some texture dependence on sample position. For the three samples, there is a correlation between SEM texture, full width at half-maximum of rocking curves and J_c versus temperature curves.

I. INTRODUCTION

Since the discovery of cuprate high temperature superconductors (HTS) by Bednorz and Muller¹ in 1986, a large number of investigations have been devoted to the development of HTS thin film deposition.² Of particular importance are the issues of surface roughness and the difficulties of fabricating large area, mirror smooth films with uniform physical properties. In general, smooth surfaces can be produced only if medium temperature deposition processes are used. The substrate temperature during deposition significantly influences the critical temperature T_c .³ The substrate temperature also strongly influences the orientation of the film crystal structure relative to the crystal plane of the substrate.³ Substrate temperature, deposition rate, and film composition all influence surface smoothness.⁴ For large area HTS films all of these factors must be well controlled to achieve high quality films for a variety of electronic applications.

Obviously, it is important to use a deposition technique which is able to produce single crystal HTS films on a wide range of substrate materials, especially those which do not have an ideal lattice match with 123 type ceramics. It has been known for some time that ionized cluster beam (ICB) deposition allows epitaxial film growth to be achieved even in cases of large lattice mismatch.⁵ Therefore, the recent application of ICB deposition to the fabrication of 123 type films is a logical development in HTS thin film research.⁶ At this time, it is of interest to survey some physical properties of ICB deposited 123 films since these films have good prospects for thin film electronic device applications.⁷ The data

presented here concern films produced in an experimental ICB apparatus. This ICB equipment was fabricated by Mitsubishi Electric Corporation in Amagasaki, Japan, and is presently being used at the University of Colorado at Colorado Springs.

II. EXPERIMENTAL

Three ICB sources⁵ were used to deposit 123 thin films on a variety of substrate materials. The base pressure of the vacuum system was 5×10^{-9} Torr. Load-lock mechanisms were used to introduce samples into the chamber, and to reload refractory metal source crucibles. The sample holder platten was 100 mm in diameter and was heated to 650 °C by thermal radiation from Ta wire heaters located above it. During film deposition, the sample holder was rotated at 10 rpm to obtain uniform film properties. Ionization of the cluster beams was produced by electron impact, and the acceleration voltage for deposition was between 0.3 and 0.5 kV. Quartz crystal deposition monitors were used to determine the deposition rate from each source before and during deposition. The film deposition rate was 3 to 4 nm/min. A shutter was opened and closed to start and stop deposition. The substrate temperature was monitored by optical pyrometry during film deposition. The oxidation gas was composed of 6 at. % ozone in oxygen. This gas was introduced into the chamber through a narrow tube located in proximity to the substrate holder. The oxidizing gas pressure was raised to 4×10^{-4} Torr after the substrate temperature was stabilized

and held constant during deposition and during the sample cool down.

III. RESULTS

YBCO and ErBCO thin films have been deposited by ICB onto a variety of substrates. These films have very similar properties. However, Er has a vapor pressure that is significantly higher than the vapor pressure of Y at any temperature.⁸ Thus, the source temperature for the deposition of Er is significantly lower than for Y at the same deposition rate. This is an advantage for ErBCO deposition. Therefore, in this paper we will limit our discussion to ErBCO films deposited by ICB.

Figure 1 shows the resistance-temperature relationship for an ErBaCuO film on SrTiO₃(100). This curve shows essentially a linear decline of resistance until the steep drop to zero resistance at 87 K. A typical J_c versus temperature curve of an ICB deposited ErBaCuO film on SrTiO₃ is shown in Fig. 2. At 77 K, J_c is greater than 1×10^6 A/cm², and J_c increases to over 3×10^6 A/cm² at 65 K.

Some work has been done to determine the properties of large area ErBCO films. Three ErBCO films deposited simultaneously on SrTiO₃(100). The positions of the substrates on the sample holder are shown in Fig. 3. The center of sample A was 25 mm from the center of the sample holder, the center of sample B was 18 mm from the center, and sample C was centered in the holder. The films were deposited at a nominal substrate temperature of 650 °C and were 100-nm thick. These films were examined by scanning electron micrographs (SEM). The micrographs of films A, B, and C are shown in Fig. 4. As seen in these micrographs, the film structure becomes more textured as the distance to the center of the sample holder becomes smaller.

The T_c for films A, B, and C were 86.3, 84.9, and 84.8 K, respectively, as measured by the four point probe method. The widths ΔT_c of the conductor to superconductor transition were 2.1, 2.6, and 2.8 K, respectively. Zero field magne-

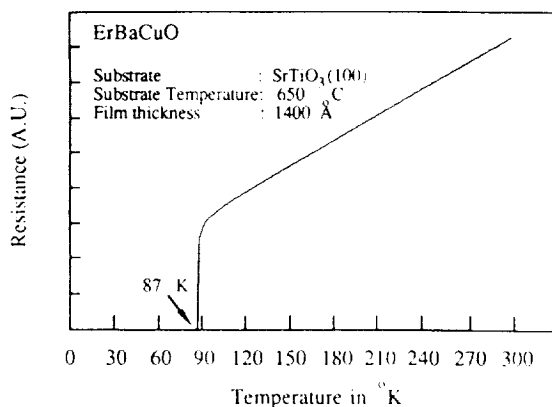


FIG. 1. Resistance-temperature curve for 100 nm thick ErBaCuO film (sample A).

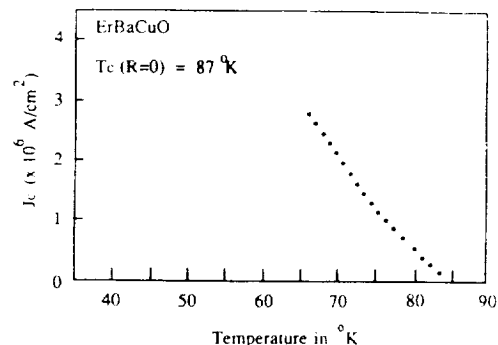


FIG. 2. Critical current density (J_c) vs temperature for an ErBaCuO film having $T_c = 87$ K.

tization (ZFC) and magnetization hysteresis measurements of these samples were made in a Quantum Design magnetic property measurement system (MPMS). All magnetization measurements were performed with the SrTiO₃ substrate face perpendicular to the applied magnetic field. The ZFC curve for sample A is shown in Fig. 5. The onset of diamagnetism occurs at approximately 85 K, in agreement with the direct current measurement of zero resistance at 86.3 K. The hysteresis curve for sample A at 4.2 K is shown in Fig. 6. The current density J_c at the temperature at which the hysteresis curve is measured can be calculated from the model of Bean.⁹ This calculation is an approximation since we are working with thin films and the Bean theory is based on cylindrical samples. However, this approach allows one to make comparisons between samples, and furthermore, the J_c calculated from hysteresis curves can be compared to direct current measurements of J_c at higher temperatures. The values of J_c versus T derived from hysteresis curves for samples A, B, and C at various temperatures are shown in Fig. 7. These values of J_c are very close except at 70 K, where J_c for sample C is significantly lower than the J_c for samples A and B. At 70 K, the calculated J_c for these samples is somewhat lower than J_c found by direct current measurements by roughly a factor of 2. However, given the approximations made to calculate J_c and the uncertainties in the sample dimensions (thickness and area), the agreement between the results found for J_c by two distinct methods is fairly good.

The x-ray spectrum of sample A is shown in Fig. 8. The x-ray diffraction spectra of samples A, B, and C are virtually identical. Since diffraction peaks only from (00 l) planes are visible in the spectra, it appears that the films have nearly

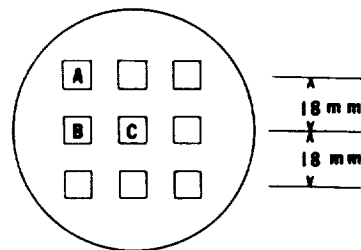


FIG. 3. Dimensions of sample holder used for samples A, B, and C.

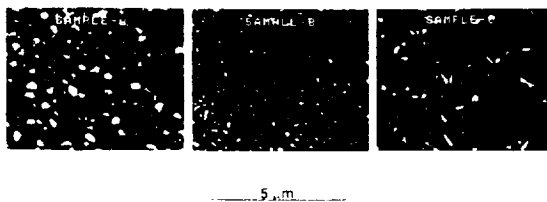


FIG. 4. SEM micrographs of a: sample A; b: sample B; c: sample C.

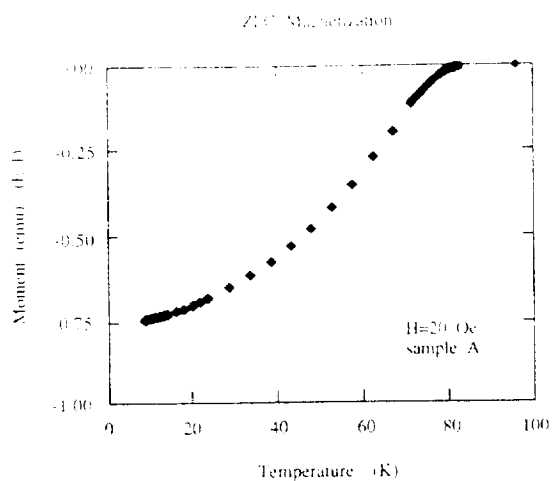


FIG. 5. Zero field cooling magnetization curve for sample A.

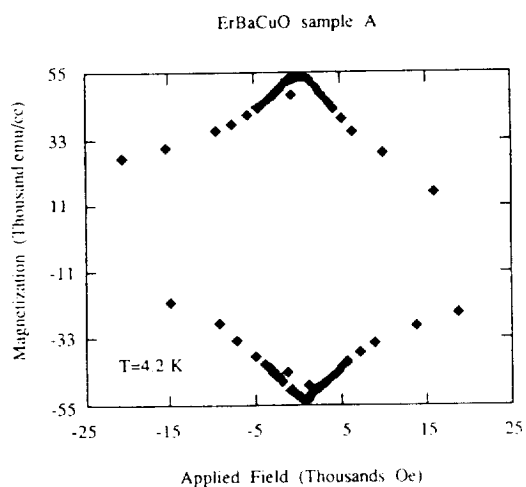


FIG. 6. Magnetization hysteresis curve at 4.2 K for sample A.

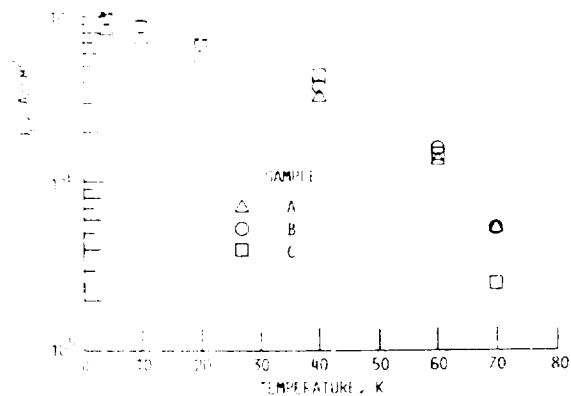


FIG. 7. DSC and thermomagnetic hysteresis curves for samples A, B, and C.

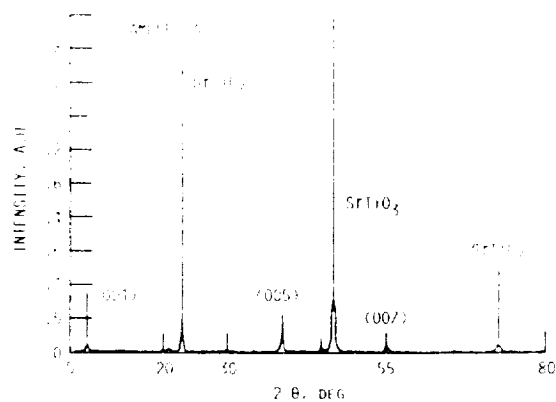


FIG. 8. X-ray spectrum of sample A. The (006) peak is hidden by the SrTiO_3 peak.

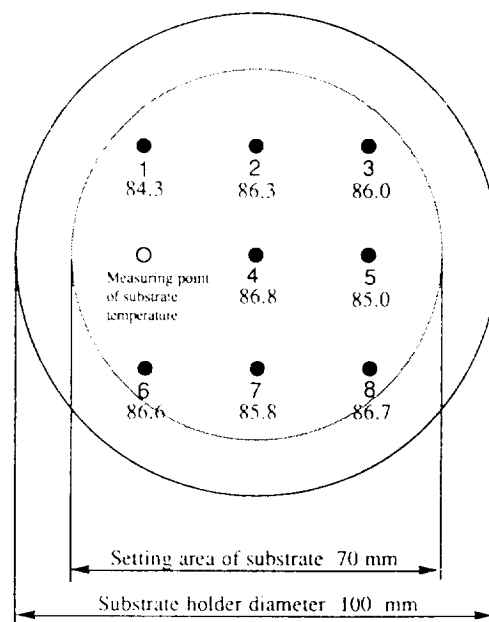


FIG. 9. Dimensions of sample holder used for large area deposition test. The values of T_c found for each sample inserted at each sample position.

Fig. 9. Location of 123 of eight ErBa₂Cu₃O_{7-x} films on SrTiO₃ substrates.

Measuring point	1	2	3	4	5	6	7	8
Measured T_c	84.3	86.3	86.0	86.8	85.0	86.6	85.8	86.7

perfect *c*-axis orientation normal to the substrate surface. However, the diffraction peaks characteristic of *a*-axis and *b*-axis growth may be obscured by the SrTiO₃ peaks. Therefore one must look for reflections, such as the (102) and (012) reflections, which do not overlap with the SrTiO₃ peaks. This type of measurement requires a four-circle diffractometer, which we have not used.

X-ray rocking curves give another indication of crystal perfection. Rocking curves were made of the (005) peaks for samples A, B, and C. These rocking curves gave full width at half-maximum (FWHM) values of 0.46°, 0.60°, and 0.63° for samples A, B, and C, respectively. It is evident that the film of sample A has a higher degree of crystal perfection than the other two samples. The x-ray rocking curve results correlate well with the higher T_c , the smaller ΔT_c , and the nominally higher J_c of sample A.

For samples A, B, and C the SEM micrographs, the x-ray rocking curves, and measured T_c and J_c show variations of film properties as a function of distance from the center of the sample holder. These variations in film properties were caused, in part, by a temperature gradient in the sample holder. Using thermocouples spot welded to the sample holder, we found a temperature 35 °C lower at the edge of the sample holder when the temperature was 650 °C at the center. Therefore, when large area HTS films are deposited, it is important to take steps to make the substrate temperature as uniform as possible.

Further information on this subject was developed by simultaneously depositing ErBa₂Cu₃O_{7-x} on eight 1 × 1 cm SrTiO₃ substrates uniformly distributed on a circular substrate holder. Figure 9 shows the center positions of the eight SrTiO₃ (100) substrates on a sample holder. The outer diameter of the substrate group was 70 mm. The measured T_c of the ErBCO films is given in Table I.

There is a 2.5 K variation in T_c for the eight samples. This variation appears to be random. This randomness may be caused by a combination of small temperature and deposition rate nonuniformities. More work is required to correlate film structure, T_c , and J_c with ICB film deposition conditions, especially for large area HTS films.

Although SrTiO₃ is an excellent substrate material for the epitaxial growth of 123 type HTS films, it has a large dielectric constant. This makes SrTiO₃ a poor candidate among substrates considered for high frequency applications of HTS films. In spite of its less than ideal lattice match with 123 films, MgO has been shown to be a good candidate as a substrate for high frequency applications.¹⁰ Another material of interest is LaAlO₃ which has a good lattice match with 123 films and good power transmission properties at millimeter wavelengths.^{10,11} ICB deposition of ErBCO films on these materials has produced T_c of 86 and 83–84 K and J_c of 3×10^5 and 1×10^5 A/cm² at 77 K on MgO(100) and

LaAlO₃(100), respectively.¹² These results were obtained for films of thickness ranging from 0.1 to 0.14 μm and deposited on 650 °C substrates. Because the number of depositions on MgO and LaAlO₃ substrates has been limited, these results should be considered as preliminary. Streaked reflection high-energy electron diffraction (RHEED) patterns from as-grown ErBCO films show that the surfaces of ErBCO films on MgO(100) substrates can be made extremely smooth by ICB deposition.¹³

IV. CONCLUSIONS

The ICB deposition of ErBa₂Cu₃O_{7-x} films on various substrates has been demonstrated to produce high quality films without need of post-annealing processes. Large area (70 mm diameter) films have been grown in a mixture of ozone and oxygen on SrTiO₃(100) at nominal substrate temperatures of 650 °C. T_c for these films are generally in the range of 84–87 K, while J_c is commonly near 1×10^5 A/m² at 77 K. Preliminary x-ray diffraction data show that the films grown on SrTiO₃ are epitaxial with the *c*-axis perpendicular to the plane of the substrate surface. However, more detailed x-ray diffraction measurements are needed to determine the proportion of *a*-axis and *b*-axis perpendicular growth. Measurements of film properties in the U.S.A. have confirmed similar measurements made at Mitsubishi Electric Corporation in Japan. Therefore, it has been established that large area, smooth, stable HTS films having high J_c and very good T_c can be routinely produced by ICB.

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TEMPERATURE DEPENDENCE OF THE ANISOTROPY IN MAGNETIC RELAXATION IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ THIN FILMS

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Abstract

The relaxation of diamagnetic magnetization in the c-axis aligned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin film is studied as a function of orientation and temperature in the range 5-50 K at $H = 0.2$ T. The magnetization $M(T, H)$ in both the orientations $H \parallel c$ and $H \perp c$ and at all the temperatures is found to decrease logarithmically with time t . An activation energy for the movement of flux lines U can be obtained using the relation $U = -kT \{1/M_0 \cdot dM/d\ln t\}^{-1}$ and is found to be 30-110 meV in the range 5-50 K. For $H \parallel c$, U increases continuously with T , where as for $H \perp c$, U has two apparent maxima: at $T = 10$ K and $T > 50$ K. These results are discussed in terms of the thermally activated flux motion model.

Introduction

Among the different magnetic properties of the high temperature superconductors, the magnetic flux relaxation or creep has been extensively studied to determine the flux pinning energy, the nature of flux line configuration and motion. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$, when $H \parallel c$, the reported values for the pinning energy in single crystals ranges from 20 meV to 17 eV and for thin films they vary from 25 meV to 4 eV.¹ The large variation is partly due to the different types of measurement techniques used. The flux relaxation and thus the pinning energy are generally discussed in terms of thermal activation combined with the various critical state models.² The flux relaxation rate for $H \perp c$ was found to be higher as compared to that for $H \parallel c$ by Rice et al.³ in disagreement with the results of Yeshurun et al.⁴ This anisotropy in relaxation has not been extensively investigated.

In this paper we report the diamagnetic relaxation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin film as a function of field orientation and temperature in the range 5-50 K. The results are discussed in terms of the thermally activated flux motion model as modified by Beasley et al.⁵ Although a qualitative explanation for the temperature variation of the activation energy U can be obtained using this model, it is found to be insufficient to explain the results completely.

Experimental Procedures

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin film (0.5 μm thick) was prepared by co-evaporation of Y, Cu and BaF_2 onto (100) SrTiO_3 substrate in an oxygen partial pressure followed by annealing in wet O_2 at 850 C. The film texture, analysed by

the standard x-ray diffraction and rocking curve techniques indicates that it is highly oriented with the c-axis perpendicular to the film plane. The grain morphology observed using scanning electron microscope shows that the grains are elongated rod like and the typical grain size is $\approx 0.5 \mu\text{m} \times 10 \mu\text{m}$. The superconducting transition temperature was determined by the dc four probe resistance method and is found to be 90 K with a transition width < 2 K.

The magnetic relaxation results reported here were obtained using the Quantum Design SQUID magnetometer. A clear plastic straw which has a negligible moment compared to the sample was used as the sample holder. In order to keep the spatial inhomogeneity in the applied field to $< 0.5 \%$ during the measurements, a short scan length of 3.6 cm is used. During each measurement, the sample was warmed up to 100 K, well above the transition temperature, and held for 5 min before cooling to the required temperature. The magnetic field was then set to the desired value, 3 min after the temperature reached a stable value ($\pm 0.5 \%$ of the set value). The magnetic relaxation data was recorded for 4000 s after the field was stabilized and a 3 min wait period.

Results and Discussion

The diamagnetic relaxation is studied as a function of temperature T and field H orientation with respect to the c-axis of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. A fixed field of 0.2 T was used in all the cases. The magnetization was found to relax logarithmically with time t (for $t > 100$ s) both for $H \parallel c$ and $H \perp c$ in the temperature range 5-50 K, indicating that the sample was in the critical state. The rate of relaxation or flux creep $dM/d\ln t$ suitably modified by the demagnetization factor is shown in fig.1(a). For both the orientations $dM/d\ln t$ has a maximum, but at different temperatures. The creep rate normalised with the initial magnetization M_0 (M at $t = 100$ s), however does not exhibit a clear maximum for either of the directions and is shown in fig.1(b). This shows that the variation of M_0 with T is significant and that it can not be ignored.

The high rates of flux creep observed in the high temperature superconductors are generally attributed to the extremely short coherence lengths, thus low energy barriers, and discussed in terms of the thermally activated flux motion

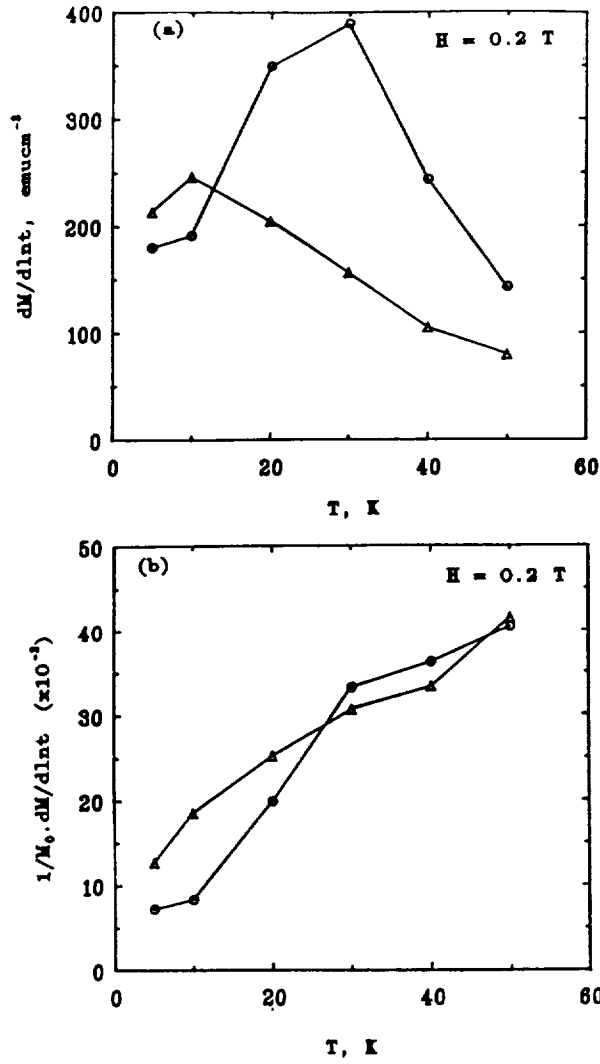


Figure 1. (a) The diamagnetic flux creep rate $dM/dlnt$ in the temperature range 5-50 K at $H = 0.2$ T. For $H \parallel c$ (Δ) the demagnetization factor $N = 0.98$ and for $H \perp c$ (\circ) $N \approx 0.6$.
(b) The normalised flux creep rate $1/M_0 \cdot dM/dlnt$; $M_0 = M(t = 100 \text{ s})$.

model. According to this model, the flux lines move as a result of the driving force which is due to the combination of flux line density gradient and thermal activation. The activation energy for flux line motion is given as,⁵ $U = -kT \{1/M_0 \cdot dM/dlnt\}^{-1}$. The activation energies for flux line motion determined using this relation are shown in fig.2.

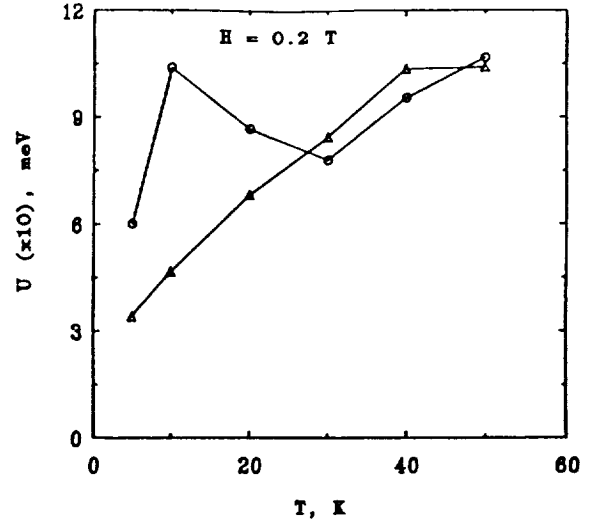


Figure 2. The activation energy $U(T)$ for $H \parallel c$ (Δ) and $H \perp c$ (\circ) at $H = 0.2$ T.
(The lines through the data points in both the figures is only an aid to the eye and does not indicate any particular behaviour).

For $H \parallel c$, U increases monotonically from ~ 34 meV at 5 K to ~ 104 meV at 40 K and saturates. This behaviour can be understood qualitatively using the formalism given in ref.5. The activation energy U is assumed to be a linear function of the driving force F and is given as $U = U_0 - FVX$, where V is the activation volume and X is the pinning length. The driving force $F \propto H \nabla B$ or HJ_c , where J_c is the critical current density at t_0 . Hence $U(T)$ can be represented as $U(T) \approx U_0(T, \nabla B) - HVXJ_c(T, \nabla B)$. The intercept U_0 is merely a tangential intercept of the true pinning potential U_p versus the field gradient ∇B curve. As the temperature increases, ∇B and J_c decrease while U_0 increases and as a consequence the observed value of U increases with T .

As mentioned earlier, the model offers only a qualitative explanation for $U(T)$. The serious limitations of the model are as follows; (i) although U_p is treated as a nonlinear function of ∇B , the net activation energy U is assumed to be a linear function of F ; (ii) the treatment is valid only in the limit $U \gg kT$, i.e. the flux line motion is only along the field gradient ∇B , which is valid only at low temperatures and high U_p ; and (iii) it does not take into account material anisotropy and variation in the pinning strengths.

For $H \perp c$, the $dM/dlnT$ curve [fig.1(a)] exhibits a peak at ≈ 30 K. This is generally interpreted as the temperature at which the flux fronts meet at the center of the sample.³ The activation energy U is found to increase with T only for $T > 30$ K, (fig.2) consistent within the description of thermally activated flux creep. However the values of U for $T < 30$ K cannot be understood even qualitatively using the above discussed model. The values of U for both the orientations are in the same range, contrary to the observation in a $YBa_2Cu_3O_7$ single crystal.⁴ A plausible reason for the low effective anisotropy is the density and type of defects in the film. Recently Daemuling et al.⁷ have reported point defects as the sources for pinning in single crystal $YBa_2Cu_3O_{7.8}$.

In conclusion, we find that the magnitude of the apparent pinning potential U is independent of the crystallographic orientation and is similar to that reported earlier.¹ In order to completely understand the nature of pinning and flux line motion, the field and temperature dependence of U together with the field dependence of the irreversibility temperature are required. The flux pinning in polycrystalline materials also depends on the method of sample preparation and hence a knowledge of the microstructure is needed to determine U_p unambiguously. Preliminary measurements of U as a function of H indicates that it decreases with increasing H ,⁸ contrary to the model proposed by Beasley et al.

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